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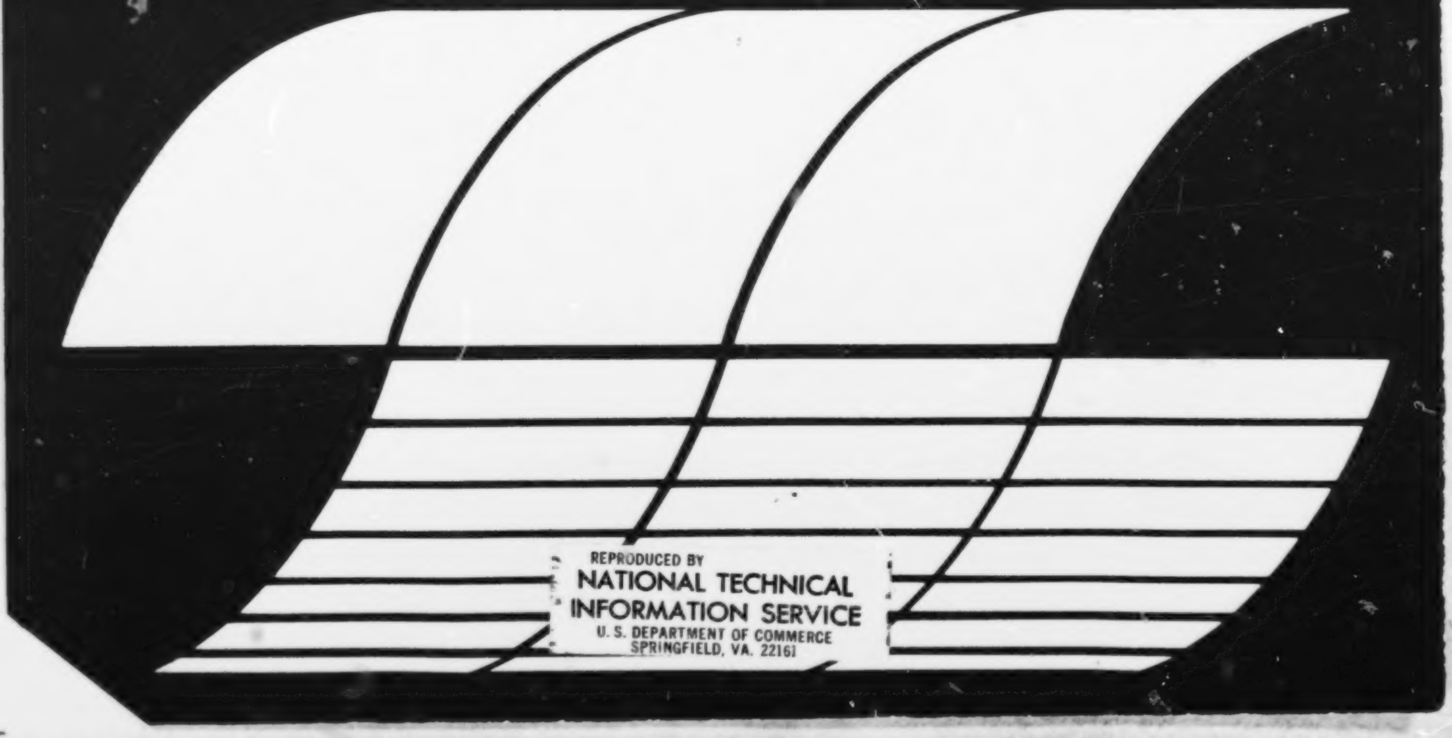

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# PROCEEDINGS: SYMPOSIUM ON FLUE GAS DESULFURIZATION— Hollywood, FL, November 1977

## (Volume II)

Franklin A. Ayer, Compiler

Research Triangle Institute
P. O. Box 12194
Research Triangle Park, N. C. 27709

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EPA Project Officer: Julian W. Jones

Industrial Environmental Research Laboratory
Office of Energy, Minerals and Industry
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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

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# PREFACE

More than half of all "man-made" sulfur dioxide ($SO_2$) is emitted by electric power plants, and the use of sulfur-containing fossil fuels, especially coal, to generate electricity is expected to increase dramatically in the next 10 years. To avoid the adverse environmental effects of this increase in fossil fuel combustion, the development and commercial application of $SO_2$ control technologies is one of the most important concerns of the U.S. Environmental Protection Agency (EPA). Flue gas desulfurization (FGD) is the most promising technique for control of $SO_2$ that will be available for widespread application to fossil fuel-fired electric power plants for at least the next 8 to 10 years.

The Industrial Environmental Research Laboratory - Research Triangle Park (IERL-RTP) of EPA's Office of Research and Development sponsors symposia for the transfer of information regarding FGD research, development and application activities with the objective of further accelerating the development and commercialization of this technology. These symposia provide an opportunity for users and developers to discuss their experiences and the status of development and application of FGD technology.

The November 1977 symposium addressed full-scale FGD process applications in the United States, Japan, and West Germany, as well as laboratory, pilot, and prototype research and development efforts. The symposium also provided an opportunity for the announcement of data and results which were previously unreported or not widely publicized. The economics of FGD and the disposal, utilization, and marketing of FGD system byproducts were also discussed. The symposium papers were presented by a cross section of those concerned with FGD including users, government and private developers, and suppliers. The electric utility industry—the principal user of FGD—participated extensively in the symposium program. More than 800 people attended the symposium.

The General Chairman of the November 1977 Symposium on Flue Gas Desulfurization was Michael A. Maxwell, Chief, Emissions/Effluent Technology Branch, IERL-RTP. The Vice Chairman was Julian W. Jones, a Chemical Engineer in the Emissions/Effluent Technology Branch, IERL-RTP.

These Proceedings are comprised of copies of the participating authors' papers as received. As supplies permit, copies of the Proceedings are available free of charge and may be obtained by contacting IERL-RTP's Technical Information Coordinator, Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

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# BY-PRODUCT DISPOSAL/UTILIZATION SESSION

Session Chairman

**Jerome Rossoff**
Director, Office of Stationary Systems
Environment and Energy Conservation Division
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# INTRODUCTION TO FGD BYPRODUCT DISPOSAL/UTILIZATION SESSION

**Jerome Rossoff**

The Aerospace Corporation
Los Angeles, California

## Introduction to FGD Byproduct Disposal/Utilization Session

Jerome Rossoff, Chairman

We have some very informative presentations this afternoon on sludge disposal and utilization technology development and on disposal applications. Before we begin I would like to review briefly the status of this technology development, and then we will bring on the speakers. One of the best ways to put the waste disposal problem in perspective is to consider the quantities of materials that will be produced. I suppose we do this from time to time to prove to ourselves that the problem isn't going away. For example, if new power plants install lime, limestone, or double alkali $SO_2$ scrubbers to meet the current standard of 1.2 pounds of $SO_2/10^6$ Btu heat input, and based on the Federal Power Commission's estimates of future electrical needs, the annual production of FGD wastes and ash from those plants in 1980 will be about 20 million tons dry, approximately half of that would be ash. In 1990 the total would be about 80 million and, by 1998, 155 million tons annually. If we assume 50 percent moisture in the wastes, then of course these values are nearly doubled.

On the other hand, if systems producing sulfur or sulfuric acid are installed in significant numbers, sludge quantities will be reduced, but the total quantity of wastes will be large. To meet current standards, for example, if half the new power plants install lime, limestone, or double alkali scrubbers between now and 1990 and the other half install acid or sulfur-producing systems, the total waste produced by those plants in 1990, instead of 80 million tons, would be approximately 60 million tons (dry), two-thirds of which would be ash. In either case, these sums represent an enormous waste disposal or utilization task.

At this time, approximately 3 million tons of sludge (dry) are produced annually. Disposal sites are in operation at 17 different power plants. Concurrently, a large research effort sponsored by the EPA and other government agencies, by EPRI, and industry itself is producing refinements in the technology of waste disposal for minimizing or eliminating environmental impact, for increasing the ability to reclaim land, for reducing the cost of disposal, and for advancing the potential for commercial utilization of these waste materials.

As we hear each time we meet, the properties, both chemical and physical, of throwaway sludges are extremely variant. A look at the existing sludge disposal techniques employed today reflects not only the fact that sludges are variable in their characteristics but that each disposal site presents highly variable conditions with regard to factors such as weather, topography, hydrology, geology, proximity to the plant, etc.

Today, there are at least half a dozen different basic approaches being used in sludge disposal operations. Some dispose of untreated sludges in unlined ponds; one converts the sludge to gypsum and disposes of it in lined ponds; others chemically treat or stabilize the sludge and dispose of it in landfills or in unlined ponds. Still others filter the sludge and further dewater it with fly ash and follow this with chemical treatment for disposal in basins or landfills. Obviously there are many approaches available, and in consideration of the environment, costs, and specific site conditions, the selection of the best approach for a particular power plant is neither obvious nor simple. The most practical choices can only be made through the use of comprehensive technical and economic data bases.

A concentrated effort to produce technical data by which improved and more economical approaches to waste disposal are developed has produced and is producing significant results toward that end. Some of these are:

1. Sludges have been characterized physically and chemically. These analyses have shown the need to avoid potential water pollution and land degradation problems.
2. Some progress has been made in relating sludge characteristics to scrubber operations; e.g., the superior dewatering and handling qualities of gypsum compared to sulfite sludges have been shown; differences in lime and limestone sludges, with and without ash, have been identified; the similarities between the properties of double alkali solids and lime sludge solids have been shown; however, the ability to control sludge characteristics through control of scrubber operating parameters needs more work,
3. Progress has been made in the development of improved dewatering methods. It now appears that a separation of the clarification and thickening functions of gravity settlers can lead to a major reduction in the size of dewatering equipment, even for sulfite sludges. The fast-settling property of gypsum has been documented, which indicates a potential major saving in equipment costs.
4. Chemical treatment benefits, effects, and estimated costs have been assessed and widely reported.
5. Cost studies have shown that dewatering and waste disposal are significant portions of total FGD costs. Process improvements such as better limestone utilization and better dewatering techniques can appreciably reduce overall costs. More work needs to be done to simplify disposal methods which would reduce disposal costs. And finally,
6. Mine disposal, especially in area surface mines, is emerging as a major disposal method. Ocean disposal is being extensively studied and may become a reasonable option in areas such as the Northeast as coal-burning is increased and where land availability may be a problem.

This list goes on and on, and unfortunately, time does not allow the presentation of results from all programs that are producing these data. An overview of some of the major programs providing specific results applicable to the general problem of waste disposal is included in this afternoon's presentations. We will hear a discussion of the economics of FGD waste disposal, a review of a waste disposal field evaluation project, two presentations on full-scale waste disposal operations using chemical treatments, a presentation on the study of mine disposal, and a presentation on the potential market for FGD byproducts. Additionally, we have a discussion of an extremely important subject: the development of regulations for FGD waste disposal. At this time, the primary Federal legislation in the area of solid waste disposal is the Resource Conservation and Recovery Act of 1976, signed into law a little over a year ago. Under the provisions of this Act, regulations governing disposal of all solid wastes will be developed by EPA or the States.

# FGD SLUDGE DISPOSAL: NEW REGULATORY INITIATIVES

**Allen J. Geswein**

U.S. Environmental Protection Agency
Washington, D.C.

# FGD Sludge Disposal: New Regulatory Initiatives

by: Allen J. Geswein

There are now a wide variety of approaches that can be employed to regulate the disposal of FGD sludge. It is possible to apply standards or regulations from Federal, State, and local agencies which have responsibilities in any of the following areas:

Solid waste disposal
Hazardous waste disposal
Wastewater disposal
Water quality criteria
Air quality criteria
Ocean disposal
Waste disposal into mines
Underground injection

However, I will discuss only the first two categories, solid and hazardous waste disposal. I will further restrict my presentation to regulations at the Federal level. The reason for these restrictions is the enactment of a new law under which EPA will be providing guidance and promulgating regulations and criteria addressing all soild waste disposal including FGD sludge disposal.

In October 1976 the Resource Conservation and Recovery Act (RCRA) became law. This Act gives the EPA, working with the States, broad powers to control the disposal of hazardous and solid wastes.

Key definitions of interest which are provided in the law are those for "solid waste" and "hazardous waste". RCRA defines "solid waste" as follows.

---

*Mr. Geswein is an Environmental Engineer in the Systems Management Division of EPA's Office of Solid Waste.

> "The term 'solid waste' means any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant, or air pollution control facility and other discarded material, including solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations, and from community activities, but does not include solid or dissolved material in domestic sewage, or solid or dissolved materials in irrigation return flows or industrial discharges which are point sources subject to permits under section 402 of the Federal Water Pollution Control Act, as amended (86 Stat. 880), or source, special nuclear or byproduct material as defined by the Atomic Energy Act of 1954, as amended (68 Stat. 923).

Also included in RCRA is the following definiton of "hazardous waste".

> "The term 'hazardous waste' means a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may--
>
>> "(A) cause, or significantly contribute tan increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or
>>
>> "(B) pose a substantial present or poetential hazard to human health or the environment when iproperly treated, stored, transported, or disposed of, or otherwise managed.

The definition of "solid waste" in RCRA specifically includes air pollution control sludges, so there is no doubt that the regulations, guidelines, and criteria promulgated under RCRA are intended to apply to FGD sludge management. Beyond this point there is very little that can be stated directly or specifically because to date no final regulations have yet been promulgated under RCRA that directly impact on FGD sludge disposal. Therefore this discussion will be confined to the current considerations for regulations, which are subject to change.

Two major categories of waste are created based on the definitions in RCRA, hazardous waste and solid waste. In general, FGD sludge is a solid waste but it or any other waste would be considered a hazardous waste if is is deemed to pose a "substantial present or potential hazard to human health or the environment" if improperly managed. Also, there is a totally different regulatory philosophy for each of the two waste categories.

## Subtitle D - Solid Waste

Subtitle D of RCRA contains the authority and mandates for non-hazardous solid waste. A principal objective of the Act is th elimination of improper disposal. Pursuant to Subtitle D, this is to be achieved primarily through State programs, but it will entail a cooperative effort among Federal, State, and local government, as well as private industry. The sequence of events called for in the Act is as follows: (1) Criteria for classification of solid waste disposal sites were to be promulgated by EPA in October 1977, (2) within one year after promulgation of the Criteria all land disposal sites are to be evaluated for compliance with the Criteria, (3) those sites not complying will be identified as open dumps in an inventory to be published in the Federal Register,

(4) following publication of the inventory the listed dumps are to be closed or upgraded to comply with the Criteria consistent with compliance schedules established by the States.

The Criteria for disposal site classification is the major guidance document to be promulgated by EPA, under Subtitle D. These criteria are to be established to determine which disposal facilities pose "no reasonable probability of adverse effects on health or the environment". Facilities which are found to not comply with the Criteria are to be classified as open dumps and are to be prohibited. The specific items to be addressed in the criteria are:

1. Environmentally sensitive areas which are wetlands, floodplains, permafrost, critical habitats, and the recharge zone for sole source aquifers..
2. Surface water quality
3. Ground water quality
4. Air quality
5. Land used for agricultural crops
6. Public health
7. Safety

Obviously, much of the responsibility for carrying out the provisions of RCRA lies with the States. RCRA contains Federal financial assistance to help support these activities. The most important element of the State control of improper disposal solid waste is the State Plan.

A State plan should (1) include provisions for resource conservation, resource recovery, and the disposal of solid waste in an environmentally sound manner, and (2) investigate and recommend which agencies and institutional arrangements are best suited for carrying out the plan. A State plan should include a statement of the current status of the State solid waste management program, the long term objectives of the State program, and a strategy and agenda for moving from current status to specific achievable objectives. Each of these elements should address the description of the institutional and organizational framework of the State and local programs, the means of control of open dumping, and the public and private processing and disposal capacities within the State.

Provisions for prohibition of open dumps is a subject area which has not been universally developed in State plans. Section 4004(b) of RCRA requires that each State plan prohibit the establishment of open dumps and contain a requirement that disposal within the State be in compliance with the criteria for disposal site classification. Section 4005(c) requires that the State plan establish a compliance schedule for open dumps which specifies a schedule of remedial measures including an enforceable sequence of actions or operations leading to compliance with the Criteria. The State plan should state the current status of the prohibition including an estimation of the compliance of the State's disposal sites pursuant to currently drafted or proposed EPA criteria at the time of plan submission. The plan should propose an acceptable goal for agency and program development which will achieve an effective prohibition. And it should express the means or approach the State will use in order to achieve reasonable certainty regarding the compliance of each of its sites. The State plan should also address the issue of the phasing of the coverage of various solid waste types such as municipal solid waste, municipal sewage sludge, hazardous wastes, non-hazardous industrial wastes, agricultural wastes and mining wastes.

In additon to requiring states to prohibit and close or upgrade open dumps, RCRA provides a Federal prohibition on open dumping. The Act does not provide for Federal enforcement of the prohibition; however, open dumps will be subject to citizen suits to obtain compliance with the Fderal prohibition.

## Subtitle C - Hazardous Waste

Under the authority of Subtitle C of RCRA, EPA is required, by April 1978, to promulgate criteria and regualtions to identify and regulate hazardous wastes. As the name implies the regulations for hazardous waste management can be expected to be more stringent and more extensive than those for other solid waste management.

The regulatory philosophy in RCRA for hazardous waste is "cradle to grave" control. EPA is to authorize State agencies to implement their own program if it is deemed equivalent to the Federally established regulations. A manifest system will be used to track the movement of hazardous waste from the point of generation through transportation, treatment, and storage, to disposal. These requirements apply to all hazardous wastes whether storage, treatment or disposal is on-site or off-site. Also inspections of these facilities are specified in RCRA. When violations of any of the regulations or permit conditions are discovered, compliance orders can be issued by EPA; and if the violator does not take corrective action, then both civil and criminal actions can be initiated.

For FGD sludges the most important regulations to be promulgated will be under Section 3001, of Subtitle C, "Identification and Listing of Hazardous Waste". Current plans are to provide criteria, test methods, and guidance to interpret the test results, as well as, lists of hazardous wastes.

A preliminary draft of criteria and methods for identifying hazardous wastes to be regulated is being circulated to a group of outside reviewers for comments. The preliminary draft has been released "for discussion purposes only" and are subject to "substantial revision", which is taking place at this time. The criteria and a description of the test method for each criteria are given below. The nature and use of lists in relation to the criteria have yet to be determined.

*Flammability* -- A waste would be flammable if a representative sample has either of the following properties; (1) any liquid waste which has a flash point less than 140°F (60°C), determined by a Pensky-Martens Closed Cup Tester, using protocol specified in ASTM Standard D-93-73; or (2) any nonfluid waste that, under conditions incident to its management, is liable to cause fires through any of a number of physical processes.

*Corrosive Wastes* -- A waste would be corrosive if a representative sample has either of the following properties: (1) any liquid waste or saturated solution of nonfluid waste having a pH less than 2 or greater than 12 as determined by an EPA-specified protocol; or (2) a corrosion rate greater than 0.250 inch per year on steel at a test temperature of 130°F, as determined by the protocol specified by National Association of Corrosion Engineers.

*Infectious Wastes* -- A waste would be infectious if it is generated from any of certain hospital departments as defined by Standard Industrial Classification codes 8062 and 8069, laboratories as defined by SIC codes 7391, 8071, and 8922, or unstabilized sewage treatment plant sludge unless these wastes do not contain micro-organisms or helminths capable of producing infection or infectious disease.

Reactive Wastes -- A waste would be reactive if it has any of the following properties: (1) a waste which is normally unstable and readily undergoes violent chemical change, but does not detonate; (2) a waste which is capable of detonation or explosive reaction, but requires strong initiating source or must be heated under confinement; or (3) a waste which is readily capable of detonation or explosive decompostion, or reacts at normal temperature and pressure. Such wastes include pyrophoric substances, explosives, autopolymerizable material and toxidizing agents.

Radioactive Wastes -- A waste would be readioactive if it is not source, special nuclear or by-product material as defined by the Atomic Energy Act of 1954, as amended, and if a representative sample has a radium 226 concentration of 3 picocuries/gram or greater, as determined by an EPA-specified mathodolgy.

Toxic Wastes -- Two methods are being considered for determining whether a waste would be deemed to be toxic. Under a bioassay test method, the entire waste would be evaluated using numerical criteria to be provided by EPA at a later date. Using an analytical test method, a waste would be analyzed to quantitatively determine its constitutents with the "hazardous" decision to be based on characteristics of the constituents. Wastes would be toxic if: (1) a concentration of any substance for which a drinking water standard exists is equal to or greater than 10 times the standard; (2) it has a concentration of any substance on the National Institute for Occupational Safety and Health toxic effect registry equal to or greater than 0.35 times the oral RAT mammalian LD 50 expressed in units of milligrams/kilogram for that substance; (3) it has a concentration of any substance equal to 10 times the lowest 96-hour TLM for that substance as listed in the NIOSH registry; (4) it meets certain phytotoxicity criteria to be provided later; (5) it contains more than an indicated amount of any genetically active material or persistent bioaccumulative material as listed in an appendix to the EPA criteria; or (6) it has a BOD/COD ratio equal to or less than a specified level and an octanol/water partition coefficient greater than or equal to a specified level.

Work is currently underway to finalize the test methods for each of the criteria. While there are many factors which will affect the selection of a specific test, the most important are listed below.

1. Environmental adequacy
2. Cost
3. Reproducibility
4. Industrial familiarity
5. Use
6. Acceptance of the method

The ultimate goal of this effort is to provide a methodology to be applied to all waste streams for the designation of solid wastes as hazardous where appropriate. It is the responsibility of those generating, transporting, treating, storing, or disposing of hazardous waste to provide notice to EPA or the State government, giving the location and a general description of the waste and the facility, within ninety (90) days after promulgation of the Section 3001 regulations. Performing the necessary tests is to be the responsibility of the owner/operator. Failure to provide the information can result in heavy fines.

## Discussion

The above has been a general description of how RCRA and subsequent regulations are expected to work. But it is appropriate to give some indication as to how this law is likely to affect the day to day operations of a power plant equipped with scrubbers.

Again I caution you that there have been no regulations from RCRA that have been finalized as yet.

From an inspection of various sources of leaching data, some tentative conclusions can be drawn regarding the overall disposal characteristics of FGD sludge. First of all, for FGD sludge, the situation which could result in environmental degradation is that FGD sludges contain relatively large quantities of heavy metals. These metals could be leached from the sludge mass and transported to ground or surface water. It is likely that this phenomenon will be the primary concern for the regulation of FGD sludge disposal. An inspection of the research data available on the leaching characteristics indicates that many heavy metals are present in the sludge mass, and given the proper conditions the metals can leach from the mass. In some cases, the concentrations of specific metals can exceed standards established by other Federal regulations. The Federal Drinking Water Standards for Barium , Cadmium , Chromium , Fluorine, and Manganese have been exceeded in leachates from FGD sludge. Due to the wide variation in the amounts of specific metals present in any given sludge, the differences in experimental methods, and the uncertainties regarding the allowable concentration of any metal, it is inappropriate to draw specific conclusions.

Since the decision to classify wastes as hazardous will be based on specific wastes and specific test results, the only conclusion to be drawn is that some FGD sludges will be classified as hazardous.

I will close with a reminder that none of these regulations have been finalized. Before any EPA regualtion can be promulgated, it is first proposed in the Federal Register for public review and comment. You should be aware that these regulations will be available for comment within the next several months though formal publication in the Federal Register and through a series of public hearings which will be held around the country. Copies of the Federal Register issue containing the proposed RCRA regulations, guidelines, and Criteria, as well as, information on the public hearings may be acquired by contacting the OSW Public Participation Officer (WH-562), U.S. EPA, 401 M Street, S.W., Washington, D.C. 20460.

# ECONOMICS OF FGD WASTE DISPOSAL

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## ABSTRACT

Several detailed studies have been conducted by TVA's Emission Control Development Projects group to evaluate the economics of lime or limestone flue gas desulfurization (FGD). In almost all of these studies, the primary emphasis has been on the scrubber system, with less emphasis placed on the disposal of solid and liquid wastes produced by the system. This report summarizes the results of studies, both complete and underway, to evaluate the economics of alternatives available to the utility industry for FGD waste disposal.

Four disposal alternatives are considered in this paper. These are: (1) untreated disposal in either ponds or landfills, (2) Dravo Corporation Synearth process used in pond or landfill systems, (3) IU Conversion System Poz-O-Tec process for landfill application, and (4) Chemfix (Division of the Carborundum Company) landfill disposal process. A base case was established for the FGD system and for each disposal process. A total of 117 variations from the base cases was considered in the evaluation of the four alternatives.

Total capital investment and annual revenue requirements were estimated for each case variation. Estimates were made so that the four alternatives could be compared for various plant, FGD system, and coal conditions.

Two additional alternatives are currently being evaluated by TVA. These are: (1) the disposal of gypsum produced by the forced oxidation of lime or limestone FGD process sludge sulfite compounds and (2) the physical stabilization of FGD sludge by mixing and blending with dry electrostatic precipitator-collected flyash. The status of this evaluation is discussed.

# ECONOMICS OF FGD WASTE DISPOSAL

## INTRODUCTION

A major problem now being faced by electric power producers using lime or limestone wet-scrubbing processes for flue gas desulfurization (FGD) is the disposal of calcium-based wastes (sludge) that are generated by the FGD system. Over 90% of the FGD systems in operation or under construction in the U.S. use the lime or limestone FGD process; however, methods for sludge disposal that are environmentally and economically acceptable are indefinite in most cases. These wastes must be disposed of within the constraints of land and water quality regulations.[1]

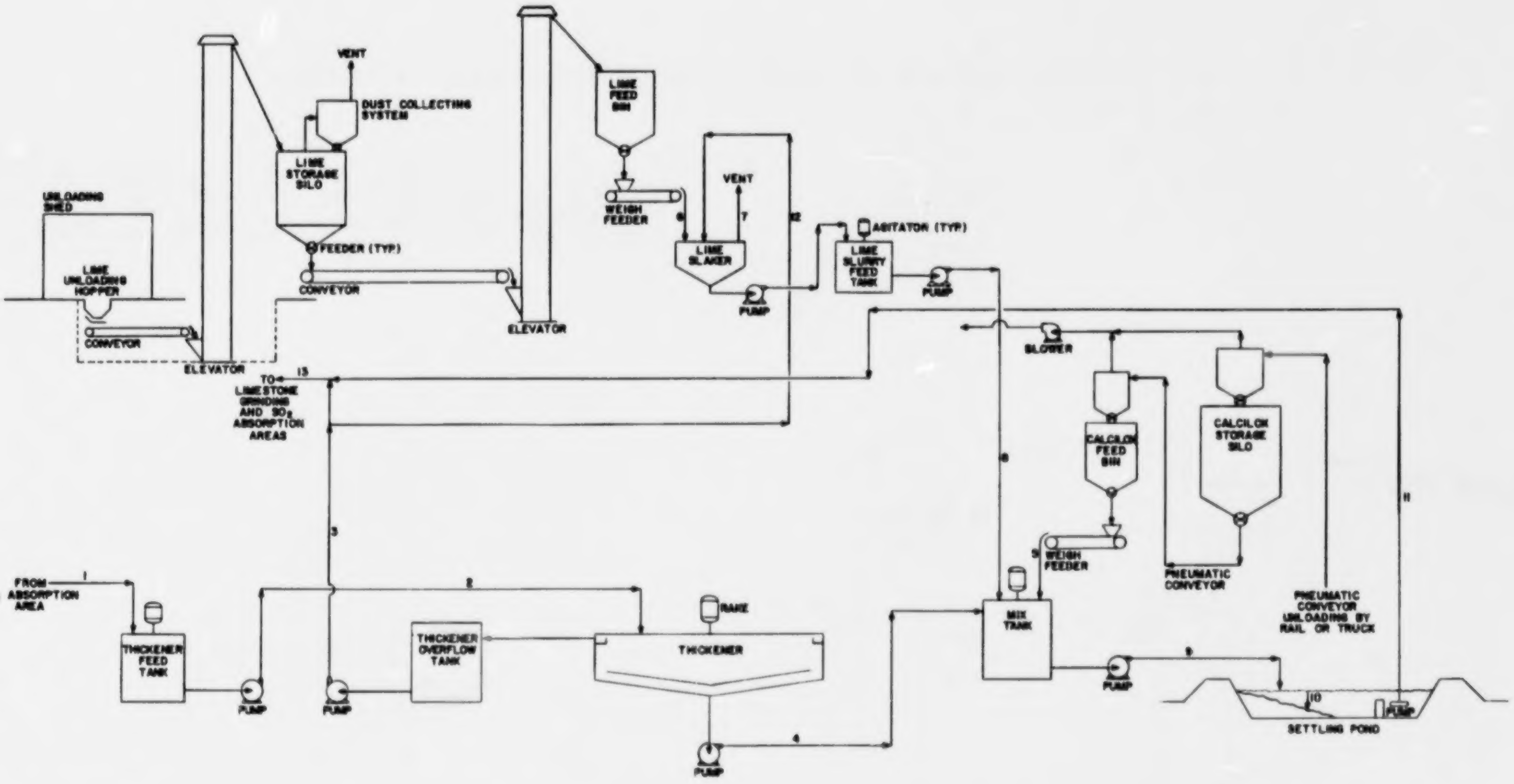
An extensive research and development program centered around sludge disposal is being funded by the U.S. Environmental Protection Agency (EPA). Projects are designed to evaluate, develop, demonstrate, and recommend environmentally and economically acceptable methods for disposal of FGD wastes. One major program area involves the economic evaluation of disposal alternatives.[2] The Tennessee Valley Authority (TVA) has been active in the economic evaluation of FGD systems for several years and in addition, has now completed the first phase of studies to evaluate sludge disposal alternatives. The results of the initial TVA sludge disposal study are discussed in this report. The objective of the work was to prepare detailed estimates of total capital investment and annual revenue requirements that are suitable for economic evaluation and comparison. Four disposal alternatives were evaluated: (1) untreated sludge disposal, (2) Dravo Corporation Synearth process, (3) IU Conversion System (IUCS) Poz-O-Tec process, and (4) Chemfix (Division of the Carborundum Company) treatment process.

## PROCESS BACKGROUND AND DESCRIPTION

There are several disposal alternatives available to the utility industry for sludge disposal, but most may be grouped into two general categories. The first category is untreated sludge disposal (disposal of sludge containing no chemical additives), with the base case being the direct ponding of scrubber system effluent (15% solids) in a lined pond. Other untreated processes include landfill disposal of dewatered and physically stabilized sludge. The second category is treated sludge disposal and includes the proprietary processes of Dravo, IUCS, and Chemfix. In all of the treatment processes, special chemical additives are used to stabilize or fix the untreated sludge. The treated material is suitable for pond or landfill disposal depending on the particular treatment process, additive rate, dewatering technique, etc. The technologies associated with the proprietary processes evaluated in this paper are assumed to be proven in full- or demonstration-scale facilities. All design parameters (equipment, additive rates, etc.) for the three systems are based on information provided by the company offering the proprietary process. Flow diagrams and material balances for these processes are shown in Figures 1 through 3.

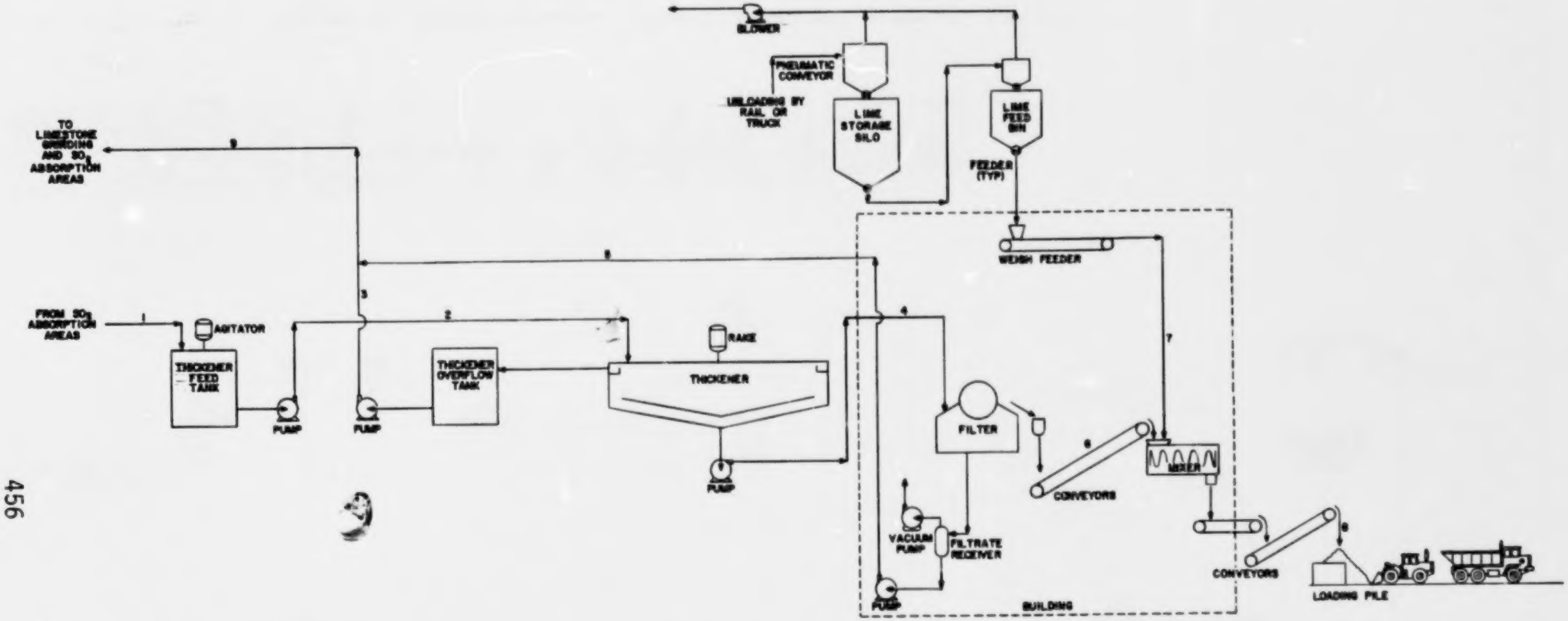
### Untreated Sludge Disposal

Direct ponding of scrubber effluent (15% solids) in a clay-lined pond is a common sludge disposal method used by the utility industry. This system, the simplest alternative, requires a minimum amount of additional equipment as compared to other disposal techniques, but the investment for a disposal pond can be very



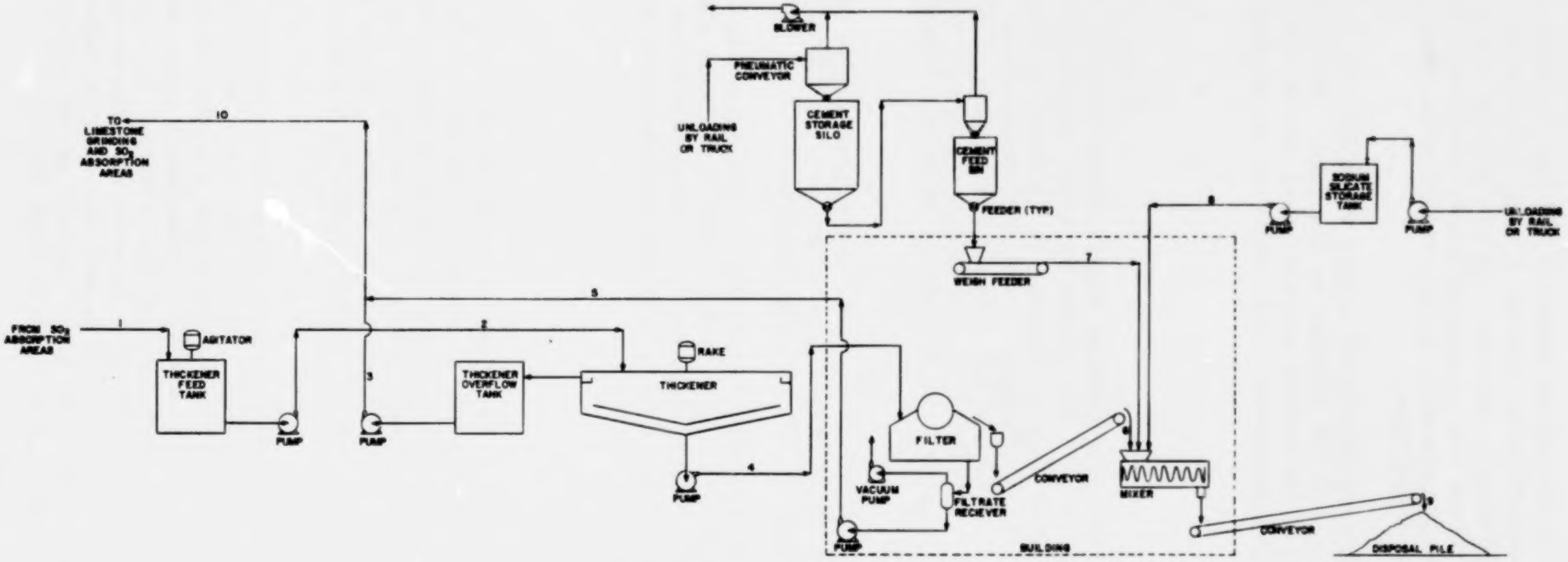
| STREAM NO | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DESCRIPTION | SLURRY TO THICKENER FEED TANK | SLURRY TO THICKENER | THICKENER OVERFLOW | UNDERFLOW TO MIX TANK | CALCILOX TO MIX TANK | LIME TO SLAKER | VENT FROM SLAKER | LIME SLURRY TO MIX TANK | USED SLURRY TO STLG POND | SETTLED USED SLURRY | RECYCLE POND WATER | RECYCLE WATER TO SLAKER | RECYCLE WATER TO SYSTEM |
| LB/HR | 772k | 772k | 441k | 331k | 8106 | 1158 | 67 | 7720 | 347k | 220k | 9/3 | 6942 | 53k |
| GPM | 1404 | 1404 | 883 | 517 | | | | 14 | 533 | 329 | 163 | 151 | 1063 |
| SP GR | 110 | 110 | | 129 | | | | 109 | 130 | 132 | | | |
| UNDSLVD SLDS % | 15 | 15 | | 35 | | | | 15 | 36 | 50 | | | |

Figure 1. Dravo process. Flow diagram and material balance.



| STREAM NO. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| DESCRIPTION | SLURRY TO THICKENER FEED TANK | SLURRY TO THICKENER | THICKENER OVERFLOW | UNDERFLOW TO FILTER | RECYCLE FILTRATE | CAKE TO MIXER | LIME TO MIXER | TREATED SLUDGE TO DISPOSAL | RECYCLE WATER TO SYSTEM |
| LB/HR | 772k | 772k | 441k | 331k | 136k | 193k | 4633 | 198k | 579k |
| GPM | 1404 | 1404 | 883 | 317 | 276 | 241 | | | 1199 |
| SP. GR. | 1.10 | 1.10 | | 1.28 | | 1.60 | | | |
| UNDSLVD SLDS. % | 15 | 15 | | 30 | | 60 | | | |

Figure 2. IUCS process. Flow diagram and material balance.



| STREAM NO. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| DESCRIPTION | SLURRY TO THICKENER FEED TANK | SLURRY TO THICKENER | THICKENER OVERFLOW | UNDERFLOW TO FILTER | RECYCLE FILTRATE | CAKE TO MIXER | CEMENT TO MIXER | SODIUM SILICATE TO MIX TANK | TREATED SLUDGE TO DISPOSAL | RECYCLE WATER TO SYSTEM |
| LB/HR | 772k | 772k | 441k | 331k | 138k | 191k | 8000 | 2102 | 203k | 579k |
| GPM | 1404 | 1404 | 883 | 517 | 276 | 241 |  | 30 |  | 1159 |
| SP GR | 110 | 110 |  | 128 |  | 150 |  | 140 |  |  |
| UNDSLVD SLDS % | 15 | 15 |  | 35 |  | 60 |  | 38 |  |  |

Fagure 3. Chemfix process. Flow diagram and material balance.

large. The ponded sludge settles to a 50% solids material and excess water is returned to the scrubber system. Some utilities are not lining the disposal pond, while others are using a variety of synthetic linings. In all ponding cases, local ground and surface water must be monitored for contamination by leachate from the disposal pond. Settled sludge is not structurally stable and is often covered with water to improve safety and aesthetic properties.

Thickeners may be used for dewatering untreated sludge (from 15% solids slurry to 35%) to reduce the quantity of material for pumping to the pond. Additional dewatering is sometimes used to yield a 60% solids material that can be handled with belt conveyors, trucks, and earthmoving equipment. This material is assumed suitable for landfill disposal.

## Dravo Process

The product for disposal is a chemically treated slurry which contains 35% solids and can be pumped to a disposal pond. The ponded material upon settling contains about 50% solids and, with 15-30 days of curing, is reported to stabilize as an earthlike material. Excess water is returned to the scrubber systems. Effluent from the scrubber system is dewatered to form a 35% solids slurry using a thickener and pumped to an agitated mix tank where Dravo's chemical fixation agents (Calcilox and Thiosorbic lime) are added. These agents and the entire fixation process are patented (called the Synearth process).[3]

The additives (Calcilox at an amount of 7% by wt of dry sludge solids and Thiosorbic lime at an amount of 2%) combine with sludge components in cementitious reactions that result in the stabilization of the sludge material.[4]

Dravo offers another process that involves intermediate ponding of treated 35% solids sludge in small (15-30 day capacity) curing ponds. The stabilized sludge is then taken from the curing ponds and is reported by Dravo to be suitable for handling with belt conveyors and can be hauled by truck to a landfill for placement and compaction.

## IUCS Process

The proprietary process offered by IUCS for stabilization of FGD sludge is marketed as the Poz-O-Tec process. Sludge is dewatered with a thickener and rotary drum filter to form a cake containing 60% solids; stabilization is then accomplished by mixing this cake with the IUCS additive lime.[5] Flyash is a necessary ingredient for stabilization and can be either removed with the sludge slurry from the precooling and scrubbing stages of the FGD process or blended with the sludge cake at the additive mixing stage of processing.

The sludge stabilization results from two sets of simultaneous reactions that occur when additives are mixed with the dewatered sludge. The first set of reactions occur over the first 24-72 hr and involves additives and soluble sulfate-sulfite compounds to produce gypsum. The second reaction begins immediately after mixing sludge and additives, but continues over a period of several months. This reaction is a cementitious phase involving pozzolanic reactions between the alumina-silica compounds of the flyash and the lime compounds. The second reaction is impeded, but not impaired by temperatures below 40°F. The water content of the mixture has a significant effect on the reactions and must be no more than 40%.[6]

The physical and chemical properties of the final product can be controlled by adjusting the additive amount, water content of sludge, and sludge composition. A material that is reported to be suitable for landfill disposal is produced from the sludge if it is dewatered to 60% solids and lime is added to the sludge (flyash is in the dewatered sludge) such that the amount is 4% by wt of dry sludge solids.[4]

IUCS reports that final product is a claylike material that can be easily handled, hauled, placed, and compacted, and that the landfill is structurally suitable for future reclamation. Surface and ground water in the area of the landfill is monitored to determine if contamination by leachate occurs.[7]

IUCS reports that their process has been successfully used for 20 yr to produce a road base material from flyash (Poz-O-Pac process). Several utilities are now using the Poz-O-Tec process in full-scale FGD sludge treatment and disposal systems.[8]

### Chemfix Process

Chemfix offers a process that yields a treated, stabilized sludge that can be handled, hauled, and placed for landfill disposal. This proprietary process uses a two-part inorganic chemical system which reacts with all polyvalent metal ions and sludge components. The slurry from the scrubber is dewatered to form a 60% solids material. The cake is then mixed with additives (sodium silicate and Portland cement) to begin the fixation reactions.

In the Chemfix system, three classes of reactions are responsible for fixation of the sludge. The first is between soluble silicates and polyvalent metal ions. The toxic trace elements, which often create a disposal problem, are tied up. The second reactions occur between the soluble silicate and the reactive components of the Portland cement. The third reactions are between the Portland cement and the sludge components.

The extent of each of these reactions influences the characteristics of the final product. For the sludge in this study, Chemfix reports that the material produced is a chemically and physically stable material suitable for landfill disposal. Sodium silicate is added such that the amount is 4% by wt of dry sludge solids and Portland cement, 7%. These rates are varied to yield desirable product characteristics.

Chemfix has been applying this technology to sludges produced by metal finishing, automotive assembly, sewage treatment, and electronics operations. Demonstration-scale applications of the process technology have been made to the stabilization of FGD sludge.[9]

## DESIGN AND ECONOMIC PREMISES

A comparative economic evaluation of several sludge disposal process systems requires that the basis for all processes be a specific set of design and economic premises. These design and economic premises, which encompass the power plant, scrubber system, and sludge disposal system are summarized in the following paragraphs.

## Base Case Design Premises

A base case was established for the power plant, FGD system, and four sludge disposal alternatives. A listing of the base case power plant premises is as follows:

1. New plant with 30-yr life.
2. Single 500-MW, coal-fired unit.
3. Total operating life of 127,500 hr with average annual capacity of 4,250 hr.
4. Power unit input heat requirement of 9000 Btu/kWh.
5. Coal heating value of 10,500 Btu/lb.
6. Coal analysis (wt %): 3.5% sulfur (S) (dry), 16.0% ash.

The following is a list of FGD system base case premises:

1. Limestone scrubbing process with 1.5 stoichiometry based on $SO_2$ removed.
2. $SO_2$ removed to meet New Source Performance Standards (NSPS).
3. Eighty percent of the ash present in the coal is emitted as flyash.
4. Ninety-five percent of the S in the coal is emitted as $SO_2$.
5. Fifteen percent of the $SO_2$ removed is converted to gypsum.
6. Flyash and $SO_2$ are removed simultaneously in the scrubber system.
7. Effluent from the FGD system is 15% solids.

The following is a listing of base case premises for the four disposal alternatives.

### Untreated

1. Pump 15% solids slurry to a clay-lined disposal pond.
2. Pond located 1 mi from scrubber facilities.
3. Sludge settles in pond to 50% solids and excess water is recycled to the scrubber system.

### Dravo

1. Thickened sludge (35% solids) is treated with Dravo additives: Calcilox (7% of dry sludge) and Thiosorbic lime (2% of dry solids).
2. A gravity thickener is used for dewatering the sludge.

3. Treated sludge is pumped to a clay-lined pond located 1 mi from the scrubber facilities.

4. The ponded sludge settles in the pond to 50% solids and excess water is recycled to the scrubber system.

5. The treated settled sludge fixes as a soillike material in the pond.

### IUCS

1. Effluent from the scrubber system is dewatered (60% solids) using a thickener and rotary drum filter.

2. The dewatered sludge is fixed by mixing with lime (4% of dry sludge).

3. Trucks are used to transport the treated sludge to the landfill disposal site located 1 mi from the scrubber facilities.

4. The treated material is assumed to have claylike properties and can be placed and compacted in the landfill using earthmoving equipment.

### Chemfix

1. Effluent from the scrubber system is dewatered (60% solids) using a thickener and rotary drum filter.

2. Dewatered sludge is fixed by mixing with Chemfix additives: Portland cement (7% of dry solids) and sodium silicate (4% of dry solids).

3. Thickened sludge (35% solids) is pumped 1 mi to the disposal site where it is filtered to remove additional water and mixed with additives.

4. The treated material is then hauled to the landfill, placed and compacted using typical earthmoving equipment.

## Design Premises and Case Variations

Design premises are the same for all alternatives, making the basis for comparison equal. The following is a summary of these assumptions.

1. Three plant sizes are considered--200, 500 (the base case), and 1500 MW. The 1500-MW plant is assumed to be three 500-MW units.

2. S in coal is 3.5% for the base case. Two alternative cases include 2.0 and 5.0% S.

3. The base case ash content of the coal is 16%. Case variations for 12 and 20% ash are also evaluated for each alternative.

4. Case variations are considered for existing 5-, 10-, and 15-yr-old plants with operating lives of 92,500 hr (5 yr), 57,500 hr (20 yr), and 32,500 hr (15 yr).

5. All estimates are based on emission standards for new steam generating facilities. The allowable $SO_2$ emission is 1.2 lb/MBtu (M = one million) heat input and the particulate standard is 0.1 lb/MBtu heat input.

6. A limestone FGD system is used for $SO_2$ removal. Flyash is removed in the scrubber system also. Case variations are estimated for (1) systems with separate flyash removal facilities--electrostatic precipitator (ESP), and (2) systems using a lime slurry FGD process.

7. Limestone systems are operated at a stoichiometry of 1.5 mol CaO:1 mol $SO_2$ removed and lime systems at a stoichiometry of 1.1 mol CaO:1 mol $SO_2$ removed.

8. Scrubber system spent slurry is assumed to contain 15% by wt solids from the limestone systems and 10% by wt from the lime systems.

9. S compounds contained in the sludge are assumed to be primarily calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2H_2O$), and gypsum (15% of the total $SO_2$ removed being converted to $CaSO_4 \cdot 2H_2O$).

10. All raw materials used in the three proprietary processes for fixation are received by rail or truck transportation. Storage facilities are for 30-day capacity; feed bins, intermediate storage tanks, etc., are 8-hr capacity.

## Economic Premises[10]

A midwestern plant location was selected. Raw materials are readily available and a large amount of coal-fired generating capacity exists in this region. Land costs are assumed $3500/acre. Economic assumptions are summarized as follows:

1. All capital cost estimates are based on Chemical Engineering cost indexes (labor index--237.9, material index--264.9). Capital costs are projected to mid-1979 and revenue requirements are for mid-1980. The project is assumed to start in mid-1977 and be completed in mid-1980. The midpoint of construction costs is mid-1979; startup, mid-1980.

2. Direct capital costs cover process equipment, piping and insulation, transport lines, foundations and structural, excavation and site preparation, roads and railroads, electrical, instrumentation, buildings, pond construction, and earthmoving equipment. Material and labor (fabrication and installation) costs for each of these items were estimated. These estimates are based on costs obtained from vendors (equipment companies, contractors, internal TVA sources, etc.,) and related literature information.

3. Indirect capital costs include engineering design and supervision, architect and engineering contractor expenses, construction expenses, contractor fees, contingency, allowance for startup and modifications, and interest during construction. Two other capital cost items, working capital and land, are included in the total capital requirements. These estimates are based on current industry practice and authoritative literature sources.

4. Direct costs for revenue requirements include raw materials, labor, electricity, and maintenance. Other direct costs are operating expenses for earthmoving equipment.

5. Indirect costs for revenue requirements are capital charges and overheads.

6. Capital charges are based on regulated utility economics.

7. Revenue requirements are projected for an annual 7,000-hr operation. Other estimates for lifetime (125,700 hr) revenue requirements are based on the declining operating time for the plant. Also estimates are made for constant annual operating loads (7,000 and 5,000 hr) throughout the life of the plant.

## RESULTS

In past TVA studies[10] estimates of total capital investment and annual revenue requirements have been made for several FGD systems. The limestone wet-scrubbing process has been evaluated in several studies and recent estimates are available that are being presented at this symposium in another TVA paper. The total capital investment for a system to be used by a 500-MW plant in 1979 (base case conditions) is estimated at $36,368,000, and the 1980 total annual revenue requirement is estimated at $11,841,500. These costs do not include the waste disposal area normally included in the system estimate and can be combined with the base case sludge disposal system costs given in this study to give the cost of a total system concept for the limestone scrubbing FGD process. It should be noted that these FGD system cost estimates apply only to the base case systems.

Design premises for the power plant, FGD system, and the four primary disposal alternatives were used to develop material balances, flow diagrams, equipment description lists, instrumentation diagrams, and overall plant layout drawing for each alternative. This information and the economic premises were used in preparing estimates of the total capital investment for each system. Case variations were considered for each of the four primary alternatives resulting in a total of 121 estimates. These case variations included power plant size, remaining plant life, coal analysis, distance from scrubbing facility to disposal area, transportation mode, sludge composition, and fixation additive rates.

Information obtained from process and equipment vendors, utility companies, and authoritative literature sources was used to estimate the costs for equipment, labor, maintenance, raw materials, cost of capital, and energy. Tables 1 and 2 are summaries of the total capital investment and annual revenue requirements for the 121 estimates. Tables 3 through 6 show capital investment analysis for each process (200-, 500-, and 1500-MW plants).

### Total Capital Investment and Annual Revenue Requirements

The relative ranking of the total capital investments for the four base case disposal alternatives is as follows:

| | Total capital investment, $ | $/kW |
|---|---|---|
| IUCS | 10,717,000 | 21.4 |
| Chemfix | 13,531,000 | 27.1 |
| Untreated | 17,211,000 | 34.4 |
| Dravo | 24,114,000 | 48.2 |

## TABLE 1. SUMMARY OF TOTAL CAPITAL INVESTMENT[a]

## ALL PROCESSES

| Case | Untreated | | Dravo | | IUCS | | Chemfix | |
|---|---|---|---|---|---|---|---|---|
| | k$ | $/kW | k$ | $/kW | k$ | $/kW | k$ | $/kW |
| Base case[b] | 17,211[c] | 34.4[c] | 24,114[d] | 48.2[d] | 10,717[e] | 21.4[e] | 13,531[f] | 27.1[f] |
| Variation from base case | | | | | | | | |
| 200 MW new | 9,800 | 49.0 | 13,942 | 69.7 | 7,193 | 36.0 | 9,259 | 46.3 |
| 200 MW existing, 25 yr remaining life | 8,480 | 42.4 | 13,258 | 66.3 | 7,428 | 37.1 | 9,448 | 47.2 |
| 200 MW existing, 20 yr remaining life | 6,844 | 34.2 | 11,597 | 58.0 | 7,351 | 36.8 | 9,367 | 46.8 |
| 200 MW existing, 15 yr remaining life | 5,511 | 27.6 | 10,239 | 51.2 | 7,295 | 36.5 | 9,311 | 46.5 |
| Existing, 25 yr remaining life | 14,578 | 29.2 | 21,416 | 42.8 | 10,591 | 21.2 | 13,400 | 26.8 |
| Existing, 20 yr remaining life | 11,399 | 22.8 | 18,281 | 36.6 | 10,402 | 20.8 | 13,204 | 26.4 |
| Existing, 15 yr remaining life | 8,822 | 17.6 | 15,553 | 31.1 | 10,269 | 20.5 | 13,077 | 26.2 |
| 1500 MW new | 36,455 | 24.3 | 48,235 | 32.2 | 20,105 | 13.4 | 24,104 | 16.1 |
| 1500 MW existing, 25 yr remaining life | 30,212 | 20.1 | 41,382 | 27.6 | 19,952 | 13.3 | 23,922 | 15.9 |
| 1500 MW existing, 20 yr remaining life | 22,904 | 15.3 | 33,924 | 22.6 | 19,382 | 12.9 | 23,337 | 15.6 |
| 1500 MW existing, 15 yr remaining life | 16,999 | 11.3 | 27,905 | 18.6 | 18,976 | 12.7 | 22,915 | 15.3 |
| 12% ash in coal | 15,031 | 30.1 | 21,446 | 42.9 | 9,345 | 18.7 | 11,879 | 23.8 |
| 20% ash in coal | 19,055 | 38.1 | 26,028 | 52.1 | 11,957 | 23.9 | 14,192 | 28.4 |
| 2% sulfur in coal | 13,390 | 26.8 | 19,251 | 38.5 | 9,025 | 18.1 | 11,123 | 22.2 |
| 5% sulfur in coal | 20,655 | 41.3 | 28,523 | 57.0 | 12,283 | 24.6 | 14,854 | 29.7 |
| 200 MW, no flyash | 6,716 | 33.6 | 12,242 | 61.2 | 7,301 | 36.5 | 7,767 | 38.8 |
| No flyash | 11,397 | 22.8 | 19,745 | 39.5 | 9,839 | 19.7 | 10,124 | 20.2 |
| 1500 MW, no flyash | 23,595 | 15.7 | 38,722 | 25.8 | 18,103 | 12.1 | 18,313 | 12.2 |
| 5 mi to disposal | 26,836 | 53.7 | 30,994 | 62.0 | 11,377 | 22.8 | 20,227 | 40.5 |
| 10 mi to disposal | 37,420 | 74.8 | 37,765 | 75.5 | 11,891 | 23.8 | 26,988 | 54.0 |
| Fixation additive amount - variation 1 | - | - | 23,120 | 46.2 | 10,302 | 20.6 | 16,270 | 32.5 |
| Fixation additive amount - variation 2 | - | - | 25,209 | 50.4 | 10,748 | 21.5 | 14,757 | 29.5 |
| Lime scrubbing process | 16,226 | 32.5 | 21,318 | 42.6 | 10,383 | 20.8 | 12,431 | 24.9 |
| Intermediate ponding and truck to landfill | - | - | 12,670 | 25.3 | - | - | - | - |
| Transport by truck to disposal area | - | - | - | - | - | - | 11,740 | 23.5 |
| Clarify (35% solids) and pump 1 mi | 18,490 | 37.0 | - | - | - | - | - | - |
| Clarify (35% solids) and pump 5 mi | 24,881 | 49.8 | - | - | - | - | - | - |
| Clarify (35% solids) and pump 10 mi | 31,458 | 62.9 | - | - | - | - | - | - |
| Clarify, filter (60% solids) and truck 1 mi | 8,294 | 16.6 | - | - | - | - | - | - |
| Clarify, filter (60% solids) and truck 5 mi | 8,825 | 17.7 | - | - | - | - | - | - |
| Clarify, filter (60% solids) and truck 10 mi | 9,249 | 18.5 | - | - | - | - | - | - |
| 200 MW, constrained pond acreage (50% of optimum) | 12,774 | 63.9 | 20,701 | 103.5 | - | - | - | - |
| 200 MW, constrained pond acreage (75% of optimum) | 10,203 | 51.0 | 17,305 | 86.5 | - | - | - | - |
| Constrained pond acreage (50% of optimum) | 22,676 | 45.4 | 37,697 | 75.4 | - | - | - | - |
| Constrained pond acreage (75% of optimum) | 17,985 | 36.0 | 31,061 | 62.1 | - | - | - | - |
| 1500 MW constrained pond acreage (50% of optimum) | 48,917 | 32.6 | 80,098 | 53.4 | - | - | - | - |
| 1500 MW constrained pond acreage (75% of optimum) | 38,228 | 25.5 | 64,503 | 43.0 | - | - | - | - |
| Pond settled density (40% solids) | 20,070 | 40.1 | - | - | - | - | - | - |
| Pond settled density (60% solids) | 15,194 | 30.4 | - | - | - | - | - | - |
| Unlined pond | 14,391 | 28.8 | - | - | - | - | - | - |
| Synthetic pond lining ($1.50/yd$^2$) | 20,994 | 42.0 | - | - | - | - | - | - |
| Synthetic pond lining ($2.50/yd$^2$) | 23,070 | 46.1 | - | - | - | - | - | - |
| Synthetic pond lining ($3.50/yd$^2$) | 24,959 | 49.9 | - | - | - | - | - | - |
| Synthetic pond lining ($4.50/yd$^2$) | 26,707 | 53.4 | - | - | - | - | - | - |

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a. Basis: Midwest plant location, mid-1979 costs; $SO_2$ and flyash removed together to meet NSPS.

b. New 500-MW plant; 30-yr life; coal analysis (by wt): 3.5% S (dry basis), 16% ash; flyash and $SO_2$ removed together to meet NSPS, limestone process with 1.5 stoichiometry based on $SO_2$ removed.

c. Direct ponding of 15% slurry clay-lined pond; 1 mi from scrubber facilities; 50% solids settled density.

d. Ponding of 35% solids slurry; clay-lined pond; pump 1 mi to pond from scrubber facilities; 50% solids settled density in pond; treated with Calcilox (7% of dry sludge) and Thiosorbic lime (1% of dry sludge).

e. Landfill disposal of 60% solids material; 1 mi to landfill from scrubber facilities; trucks used for transport of treated sludge; treated with lime (4% of dry sludge).

f. Landfill disposal of 60% solids material; 1 mi to landfill from scrubber facilities; pipeline used for transport of thickener underflow to disposal and treatment area, treated with Portland cement (7% of dry sludge) and sodium silicate (2% of dry sludge).

# TABLE 2. SUMMARY OF TOTAL ANNUAL REVENUE REQUIREMENTS[a]

## ALL PROCESSES

| | Untreated | | Dravo | | IUCS | | Chemfix | |
|---|---|---|---|---|---|---|---|---|
| Case | Annual amount, k$ | Mills/ kWh | Annual amount, k$ | Mills/ kWh | Annual amount, k$ | Mills/ kWh | Annual amount, k$ | Mills/ kWh |
| Base case[b] | 3,280[c] | 0.94[c] | 6,701[d] | 1.91[d] | 5,291[e] | 1.51[e] | 6,988[f] | 2.00[f] |
| Variation from base case | | | | | | | | |
| 200 MW new | 2,014 | 1.44 | 3,643 | 2.60 | 3,567 | 2.55 | 4,529 | 3.24 |
| 200 MW existing, 25 yr remaining life | 1,841 | 1.32 | 3,672 | 2.62 | 3,699 | 2.64 | 4,695 | 3.35 |
| 200 MW existing, 20 yr remaining life | 1,605 | 1.15 | 3,461 | 2.47 | 3,725 | 2.66 | 4,730 | 3.38 |
| 200 MW existing, 15 yr remaining life | 1,433 | 1.02 | 3,390 | 2.42 | 3,822 | 2.73 | 4,856 | 3.47 |
| Existing 25 yr remaining life | 2,906 | 0.83 | 6,377 | 1.82 | 5,402 | 1.54 | 7,152 | 2.04 |
| Existing 20 yr remaining life | 2,135 | 0.70 | 5,941 | 1.70 | 5,430 | 1.55 | 7,191 | 2.05 |
| Existing 15 yr remaining life | 2,130 | 0.61 | 5,728 | 1.64 | 5,559 | 1.59 | 7,359 | 2.10 |
| 1500 MW new | 6,746 | 0.64 | 14,264 | 1.36 | 10,411 | 0.99 | 14,362 | 1.37 |
| 1500 MW existing, 25 yr remaining life | 5,827 | 0.55 | 13,821 | 1.32 | 10,656 | 1.01 | 14,749 | 1.40 |
| 1500 MW existing, 20 yr remaining life | 4,726 | 0.45 | 12,749 | 1.21 | 10,684 | 1.02 | 14,791 | 1.41 |
| 1500 MW existing, 15 yr remaining life | 3,969 | 0.38 | 12,138 | 1.16 | 10,900 | 1.04 | 15,053 | 1.43 |
| 12% ash in coal | 2,902 | 0.83 | 5,924 | 1.69 | 4,533 | 1.30 | 6,229 | 1.78 |
| 20% ash in coal | 3,609 | 1.03 | 7,406 | 2.12 | 5,971 | 1.71 | 7,600 | 2.17 |
| 2% sulfur in coal | 2,639 | 0.75 | 5,314 | 1.52 | 4,654 | 1.33 | 5,935 | 1.70 |
| 5% sulfur in coal | 3,869 | 1.10 | 8,007 | 2.29 | 6,188 | 1.77 | 8,263 | 2.36 |
| 200 MW, no flyash | 1,495 | 1.07 | 3,063 | 2.19 | 3,396 | 2.43 | 3,766 | 2.69 |
| No flyash | 2,289 | 0.65 | 5,073 | 1.45 | 4,650 | 1.33 | 5,184 | 1.48 |
| 1500 MW, no flyash | 4,546 | 0.43 | 10,448 | 1.00 | 8,162 | 0.78 | 9,771 | 0.93 |
| 5 mi to disposal | 5,527 | 1.58 | 8,124 | 2.32 | 6,490 | 1.85 | 8,675 | 2.48 |
| 10 mi to disposal | 7,504 | 2.14 | 9,360 | 2.67 | 7,475 | 2.14 | 10,003 | 2.86 |
| Fixation additive rate - variation 1 | - | - | 6,052 | 1.73 | 4,994 | 1.43 | 13,651 | 3.90 |
| Fixation additive rate - variation 2 | - | - | 7,577 | 2.16 | 5,511 | 1.57 | 10,099 | 2.89 |
| Lime scrubbing process | 3,136 | 0.90 | 6,168 | 1.76 | 5,093 | 1.46 | 6,200 | 1.77 |
| Intermediate ponding and truck to landfill | - | - | 6,620 | 1.89 | - | - | - | - |
| Transport by truck to disposal area | - | - | - | - | - | - | 6,698 | 1.91 |
| Clarify (35% solids) and pump 1 mi | 3,694 | 1.06 | - | - | - | - | - | - |
| Clarify (35% solids) and pump 5 mi | 5,195 | 1.48 | - | - | - | - | - | - |
| Clarify (35% solids) and pump 10 mi | 6,450 | 1.84 | - | - | - | - | - | - |
| Clarify, filter (60% solids) and truck 1 mi | 3,809 | 1.09 | - | - | - | - | - | - |
| Clarify, filter (60% solids) and truck 5 mi | 4,925 | 1.41 | - | - | - | - | - | - |
| Clarify, filter (60% solids) and truck 10 mi | 5,818 | 1.66 | - | - | - | - | - | - |
| 200 MW, constrained pond acreage (50% of optimum) | 2,462 | 1.76 | 4,423 | 3.16 | - | - | - | - |
| 200 MW, constrained pond acreage (75% of optimum) | 2,033 | 1.45 | 4,134 | 2.95 | - | - | - | - |
| Constrained pond acreage (50% of optimum) | 4,119 | 1.18 | 9,109 | 2.60 | - | - | - | - |
| Constrained pond acreage (75% of optimum) | 3,365 | 0.96 | 7,901 | 2.25 | - | - | - | - |
| 1500 MW, constrained pond acreage (50% of optimum) | 8,985 | 0.86 | 20,366 | 1.94 | - | - | - | - |
| 1500 MW, constrained pond acreage (75% of optimum) | 7,037 | 0.67 | 17,290 | 1.65 | - | - | - | - |
| Pond settled density(40% solids) | 3,747 | 1.07 | - | - | - | - | - | - |
| Pond settled density(60% solids) | 2,949 | 0.84 | - | - | - | - | - | - |
| Unlined pond | 2,765 | 0.79 | - | - | - | - | - | - |
| Synthetic pond lining ($1.50/yd$^2$) | 3,882 | 1.11 | - | - | - | - | - | - |
| Synthetic pond lining ($2.50/yd$^2$) | 4,253 | 1.21 | - | - | - | - | - | - |
| Synthetic pond lining ($3.50/yd$^2$) | 4,590 | 1.31 | - | - | - | - | - | - |
| Synthetic pond lining ($4.50/yd$^2$) | 4,900 | 1.40 | - | - | - | - | - | - |

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a. Basis: Midwest plant location; mid-1980 operating costs; 7,000 hr/yr on-stream time.

b. New 500-MW plant; 30-yr life; coal analysis (by wt): 3.5% S (dry basis), 16% ash; flyash and $SO_2$ removed together to meet NSPS, limestone process with 1.5 stoichiometry based on $SO_2$ removed.

c. Direct ponding of 15% slurry; clay-lined pond; 1 mi from scrubber facilities; 50% solids settled density.

d. Ponding of 35% solids slurry; clay-lined pond; pump 1 mi to pond from scrubber facilities; 50% solids settled density in pond; treated with Calcilox (7% of dry sludge) and Thiosorbic lime (1% of dry sludge).

e. Landfill disposal of 60% solids material; 1 mi to landfill from scrubber facilities, trucks used for transport of treated sludge; treated with lime (4% of dry sludge).

f. Landfill disposal of 60% solids material; 1 mi to landfill from scrubber facilities; pipeline used f transport of thickener underflow to disposal and treatment area, treated with Portlant cement (7% of dry sludge) and sodium silicate (2% of dry sludge).

## TABLE 3. CAPITAL INVESTMENT ANALYSIS

## UNTREATED PROCESSES

| | Investment | | | | | |
|---|---|---|---|---|---|---|
| | 200 MW[a] | | 500 MW[a] | | 1500 MW[a] | |
| | k$ | Percent of total | k$ | Percent of total | k$ | Percent of total |
| Process equipment | 78 | 0.8 | 128 | 0.7 | 237 | 0.6 |
| Piping and insulation | 96 | 1.0 | 121 | 0.7 | 207 | 0.5 |
| Transport lines | 746 | 7.5 | 1,109 | 6.4 | 1,922 | 5.3 |
| Foundation and structural | 6 | 0.1 | 7 | 0.1 | 14 | 0.1 |
| Excavation, site preparation; roads and railroads | 66 | 0.7 | 73 | 0.4 | 77 | 0.2 |
| Electrical | 354 | 3.6 | 395 | 2.3 | 522 | 1.4 |
| Instrumentation | 41 | 0.4 | 53 | 0.3 | 53 | 0.1 |
| Buildings | - | - | - | - | - | - |
| Subtotal | 1,387 | 14.1 | 1,886 | 10.9 | 3,032 | 8.3 |
| Services and miscellaneous | 21 | 0.2 | 28 | 0.2 | 45 | 0.1 |
| Subtotal excluding pond | 1,408 | 14.3 | 1,914 | 11.1 | 3,077 | 8.4 |
| Pond construction | 3,652 | 37.3 | 7,251 | 42.2 | 16,946 | 46.5 |
| Subtotal direct investment | 5,060 | 51.6 | 9,165 | 53.3 | 20,023 | 54.9 |
| Engineering design and supervision | 262 | 2.7 | 367 | 2.1 | 587 | 1.6 |
| Architect/engineering contractor expense | 38 | 0.4 | 49 | 0.3 | 71 | 0.2 |
| Construction expense | 713 | 7.3 | 1,102 | 6.4 | 1,997 | 5.5 |
| Contractor fees | 329 | 3.3 | 517 | 3.0 | 936 | 2.6 |
| Subtotal | 6,402 | 65.3 | 11,200 | 65.1 | 23,614 | 64.8 |
| Contingency | 1,280 | 13.1 | 2,240 | 13.0 | 4,723 | 12.9 |
| Subtotal fixed investment | 7,682 | 78.4 | 13,440 | 78.1 | 28,337 | 77.7 |
| Allowance for startup and modification | 403 | 4.1 | 619 | 3.6 | 1,139 | 3.1 |
| Interest during construction | 922 | 9.4 | 1,613 | 9.3 | 3,400 | 9.4 |
| Subtotal capital investment | 9,007 | 91.9 | 15,672 | 91.0 | 32,876 | 90.2 |
| Land | 708 | 7.2 | 1,423 | 8.3 | 3,359 | 9.2 |
| Working capital | 85 | 0.9 | 116 | 0.7 | 220 | 0.6 |
| Total capital investment | 9,800 | 100.0 | 17,211 | 100.0 | 36,455 | 100.0 |

[a] Basis:
New plant (30-yr life), midwest plant location, mid-1979 costs.
Coal analysis (by wt): 3.5% S (dry basis), 16% ash.
Flyash removed with $SO_2$ to meet NSPS.
Limestone process with 1.5 stoichiometry based on $SO_2$ removed.
Pond disposal, 15% solids slurry, settled density - 50% solids, clay-lined, 1 mi from scrubber facilities.

## TABLE 4. CAPITAL INVESTMENT ANALYSIS

## DRAVO PROCESS

| | Investment | | | | | |
|---|---|---|---|---|---|---|
| | 200 MW[a] | | 500 MW[a] | | 1500 MW[a] | |
| | k$ | Percent of total | k$ | Percent of total | k$ | Percent of total |
| Process equipment | 1,405 | 10.2 | 2,272 | 9.4 | 4,363 | 9.1 |
| Piping and insulation | 179 | 1.3 | 262 | 1.1 | 424 | 0.9 |
| Transport lines | 451 | 3.2 | 657 | 2.7 | 978 | 2.0 |
| Foundation and structural | 116 | 0.8 | 313 | 1.3 | 540 | 1.1 |
| Excavation, site preparation; roads and railroads | 141 | 1.0 | 164 | 0.7 | 240 | 0.5 |
| Electrical | 795 | 5.7 | 974 | 4.0 | 1,301 | 2.7 |
| Instrumentation | 100 | 0.7 | 113 | 0.5 | 119 | 0.3 |
| Buildings | 115 | 0.8 | 115 | 0.5 | 115 | 0.2 |
| Subtotal | 3,302 | 23.7 | 4,870 | 20.2 | 8,081 | 16.8 |
| Services and miscellaneous | 50 | 0.3 | 73 | 0.3 | 121 | 0.2 |
| Subtotal excluding pond | 3,352 | 24.0 | 4,943 | 20.5 | 8,202 | 17.0 |
| Pond construction | 3,479 | 25.0 | 7,410 | 30.7 | 17,358 | 36.0 |
| Subtotal direct investment | 6,831 | 49.0 | 12,353 | 51.2 | 26,560 | 53.0 |
| Engineering design and supervision | 682 | 4.9 | 821 | 3.4 | 1,136 | 2.4 |
| Architect/engineering contractor expense | 144 | 1.0 | 162 | 0.7 | 207 | 0.4 |
| Construction expense | 1,048 | 7.5 | 1,627 | 6.7 | 2,823 | 5.9 |
| Contractor fees | 414 | 3.0 | 649 | 2.3 | 1,127 | 2.3 |
| Subtotal | 9,119 | 65.4 | 15,612 | 64.7 | 30,853 | 64.0 |
| Contingency | 1,824 | 13.1 | 3,122 | 13.0 | 6,171 | 12.8 |
| Subtotal fixed investment | 10,943 | 78.5 | 18,734 | 77.7 | 37,024 | 76.8 |
| Allowance for startup and modification | 746 | 5.4 | 1,132 | 4.7 | 1,967 | 4.1 |
| Interest during construction | 1,313 | 9.4 | 2,249 | 9.3 | 4,443 | 9.2 |
| Subtotal capital investment | 13,002 | 93.3 | 22,114 | 91.7 | 43,434 | 90.1 |
| Land | 676 | 4.8 | 1,450 | 6.0 | 3,414 | 7.0 |
| Working capital | 264 | 1.9 | 550 | 2.3 | 1,387 | 2.9 |
| Total capital investment | 13,942 | 100.0 | 24,114 | 100.0 | 48,235 | 100.0 |

a. Basis:

New plant (30-yr life), midwest plant location, mid-1979 costs.
Coal analysis (by wt): 3.5% S (dry basis), 16% ash.
Flyash removed with $SO_2$ to meet NSPS.
Limestone process with 1.5 stoichiometry based on $SO_2$ removed.
Pond disposal of treated 35% solids slurry in a clay-lined pond located 1 mi from scrubber facilities, slurry settled density - 50% solids.

## TABLE 5. CAPITAL INVESTMENT ANALYSIS

## IUCS PROCESS

| | Investment | | | | | |
|---|---|---|---|---|---|---|
| | 200 MW$^a$ | | 500 MW$^a$ | | 1500 MW$^a$ | |
| | k$ | Percent of total | k$ | Percent of total | k$ | Percent of total |
| Process equipment | 1,520 | 21.1 | 2,551 | 23.7 | 5,050 | 25.1 |
| Piping and insulation | 126 | 1.8 | 176 | 1.6 | 287 | 1.4 |
| Transport lines | - | - | - | - | - | - |
| Foundation and structural | 65 | 0.9 | 136 | 1.3 | 314 | 1.6 |
| Excavation, site preparation; roads and railroads | 94 | 1.3 | 115 | 1.1 | 180 | 0.9 |
| Electrical | 430 | 6.0 | 639 | 6.0 | 1,012 | 5.0 |
| Instrumentation | 56 | 0.8 | 70 | 0.7 | 74 | 0.4 |
| Buildings | 550 | 7.6 | 550 | 5.1 | 1,004 | 5.0 |
| Subtotal | 2,841 | 39.5 | 4,237 | 39.5 | 7,921 | 39.4 |
| Services and miscellaneous | 43 | 0.6 | 64 | 0.6 | 119 | 0.6 |
| Subtotal excluding trucks and equipment | 2,884 | 40.1 | 4,301 | 40.1 | 8,040 | 40.0 |
| Trucks and earthmoving equipment | 400 | 5.6 | 581 | 5.4 | 1,057 | 5.2 |
| Subtotal direct investment | 3,284 | 45.7 | 4,882 | 45.5 | 9,097 | 45.2 |
| Engineering design and supervision | 311 | 4.3 | 392 | 3.7 | 495 | 2.5 |
| Architect/engineering contractor expense | 78 | 1.1 | 98 | 0.9 | 124 | 0.6 |
| Construction expense | 602 | 8.3 | 839 | 7.8 | 1,410 | 7.0 |
| Contractor fees | 237 | 3.3 | 320 | 3.0 | 514 | 2.6 |
| Subtotal | 4,512 | 62.7 | 6,531 | 60.9 | 11,640 | 57.9 |
| Contingency | 902 | 12.6 | 1,306 | 12.2 | 2,328 | 11.6 |
| Subtotal fixed investment | 5,414 | 75.3 | 7,837 | 73.1 | 13,968 | 69.5 |
| Allowance for startup and modification | 501 | 7.0 | 726 | 6.8 | 1,291 | 6.4 |
| Interest during construction | 650 | 9.0 | 940 | 8.8 | 1,676 | 8.3 |
| Subtotal capital investment | 6,565 | 91.3 | 9,503 | 88.7 | 16,935 | 84.2 |
| Land | 280 | 3.9 | 676 | 6.3 | 2,030 | 10.1 |
| Working capital | 348 | 4.8 | 538 | 5.0 | 1,140 | 5.7 |
| Total capital investment | 7,193 | 100.0 | 10,717 | 100.0 | 20,105 | 100.0 |

a. Basis:

New plant (30-yr life), midwest plant location, mid-1979 costs.
Coal analysis (by wt): 3.5% S (dry basis), 16% ash.
Flyash removed with $SO_2$ to meet NSPS.
Limestone process with 1.5 stoichiometry based on $SO_2$ removed.
Landfill disposal of 60% solids material 1 mi from scrubber facilities, trucks used for transport of treated material to disposal site.

## TABLE 6. CAPITAL INVESTMENT ANALYSIS

## CHEMFIX PROCESS

| | Investment | | | | | |
|---|---|---|---|---|---|---|
| | 200 MW[a] | | 500 MW[a] | | 1500 MW[a] | |
| | k$ | Percent of total | k$ | Percent of total | k$ | Percent of total |
| Process equipment | 1,709 | 18.6 | 2,885 | 21.3 | 5,499 | 22.8 |
| Piping and insulation | 173 | 1.9 | 227 | 1.7 | 367 | 1.5 |
| Transport lines | 487 | 5.3 | 697 | 5.2 | 1,027 | 4.3 |
| Foundation and structural | 77 | 0.8 | 207 | 1.5 | 394 | 1.6 |
| Excavation, site preparation; roads and railroads | 138 | 1.5 | 162 | 1.2 | 239 | 1.0 |
| Electrical | 587 | 6.3 | 853 | 6.3 | 1,274 | 5.3 |
| Instrumentation | 87 | 0.9 | 107 | 0.8 | 119 | 0.5 |
| Buildings | 550 | 5.9 | 550 | 4.1 | 1,004 | 4.2 |
| Subtotal | 3,808 | 41.2 | 5,690 | 42.1 | 9,923 | 41.2 |
| Services and miscellaneous | 57 | 0.6 | 85 | 0.6 | 149 | 0.6 |
| Subtotal excluding trucks and equipment | 3,865 | 41.8 | 5,775 | 42.7 | 10,072 | 41.8 |
| Trucks and earthmoving equipment | 423 | 4.6 | 442 | 3.2 | 789 | 3.3 |
| Subtotal direct investment | 4,288 | 46.4 | 6,217 | 45.9 | 10,861 | 45.1 |
| Engineering design and supervision | 392 | 4.2 | 472 | 3.5 | 564 | 2.3 |
| Architect/engineering contractor expense | 98 | 1.1 | 118 | 0.9 | 141 | 0.6 |
| Construction expense | 768 | 8.3 | 1,072 | 8.0 | 1,700 | 7.1 |
| Contractor fees | 290 | 3.1 | 385 | 2.8 | 588 | 2.4 |
| Subtotal | 5,836 | 63.1 | 8,264 | 61.1 | 13,854 | 57.5 |
| Contingency | 1,167 | 12.6 | 1,653 | 12.2 | 2,771 | 11.5 |
| Subtotal fixed investment | 7,003 | 75.7 | 9,917 | 73.3 | 16,625 | 69.0 |
| Allowance for startup and modification | 658 | 7.1 | 948 | 7.0 | 1,584 | 6.6 |
| Interest during construction | 840 | 9.1 | 1,190 | 8.8 | 1,995 | 8.2 |
| Subtotal capital investment | 8,501 | 91.9 | 12,055 | 89.1 | 20,204 | 83.8 |
| Land | 284 | 3.1 | 693 | 5.1 | 2,083 | 8.6 |
| Working capital | 464 | 5.0 | 783 | 5.8 | 1,817 | 7.6 |
| Total capital investment | 9,249 | 100.0 | 13,531 | 100.0 | 24,104 | 100.0 |

a. **Basis:**
New plant (30-yr life), midwest plant location, mid-1979 costs.
Coal analysis (by wt): 3.5% S (dry basis), 16% ash.
Flyash removed with $SO_2$ to meet NSPS.
Limestone process with 1.5 stoichiometry based on $SO_2$ removed.
Landfill disposal of 60% solids material 1 mi from scrubber facilities, pipelines used for transport of 35% solids thickener underflow to treatment and disposal area.

The unit revenue requirements for the four base case estimates are as follows:

| | $/ton (dry solids) | Mills/kWh |
|---|---|---|
| Untreated | 8.08 | 0.94 |
| IUCS | 12.55 | 1.51 |
| Dravo | 15.32 | 1.91 |
| Chemfix | 16.51 | 2.00 |

These rankings are for base case systems which are for new 500-MW plants burning coal with 3.5% S and 16% ash. The relative position of the four alternatives changes for some of the case variations.

## Case Variations

The effects of the following case variations on the total capital investments and annual revenue requirements are illustrated in Figures 4 through 39.

| Case variation | Effect shown in figure No. |
|---|---|
| Power plant size | 4-9 |
| Plant size and remaining life | 10-15 |
| Power plant operating profile | 16-17 |
| Sludge rate | 18-19 |
| Coal analysis | 20-23 |
| Distance to disposal site | 24-27 |
| Remaining plant life | 28-33 |
| Available pond acreage | 34-37 |
| Type of pond liner | 38-39 |

## Lifetime Revenue Requirements--Declining Profile

Lifetime revenue requirements were calculated for three cases (200-, 500-, and 1500-MW new plants) of each disposal alternative. Table 7 presents a summary of the cumulative discounted process costs and equivalent levelized unit increase in revenue requirements over the life of the power plant for the four disposal alternatives. Lifetime levelized unit revenue requirements are slightly higher than corresponding annual unit revenue requirements due to the declining operating profile of the power plant. The average annual on-stream time over the life of the plant is 4250 hr; however, the annual revenue requirement estimates are based on 7000 hr of operating time.

## Lifetime Revenue Requirements--Constant Operating Load

In order to evaluate the effects of a nondeclining operating load, estimates were made for disposal systems (each of the four alternatives for 200-, 500-, and 1500-MW plants) operating at a constant load over the 30-yr life of the system. Estimates for these 12 cases were made for both 5000 and 7000 hr/yr operation. Tables 8 and 9 are summaries of these estimates. Both total capital investment and annual revenue requirements are increased over the corresponding values for systems with the declining operating profile.

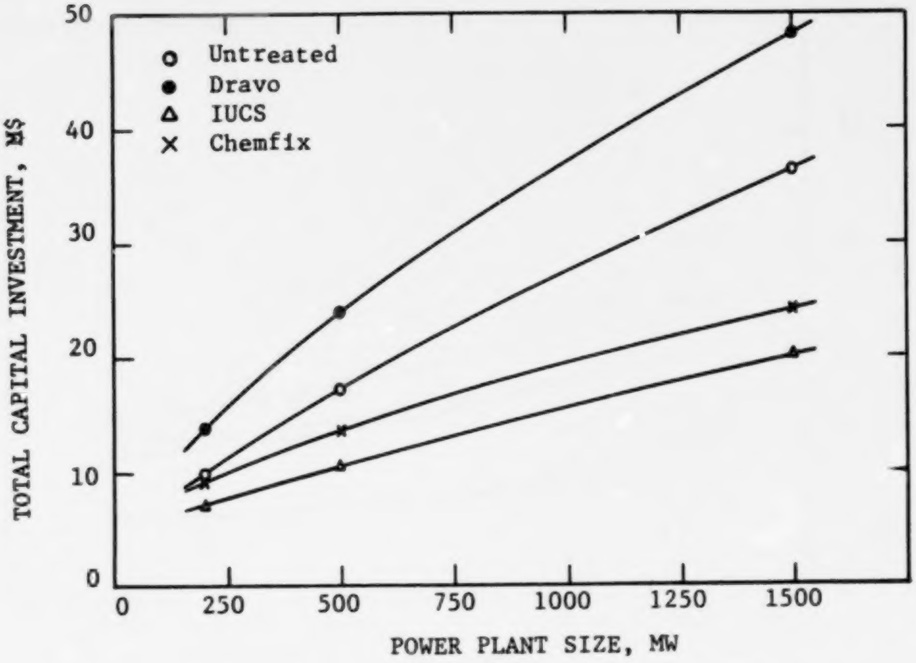

Figure 4. All processes. Effect of power plant size on total capital investment. New plants.

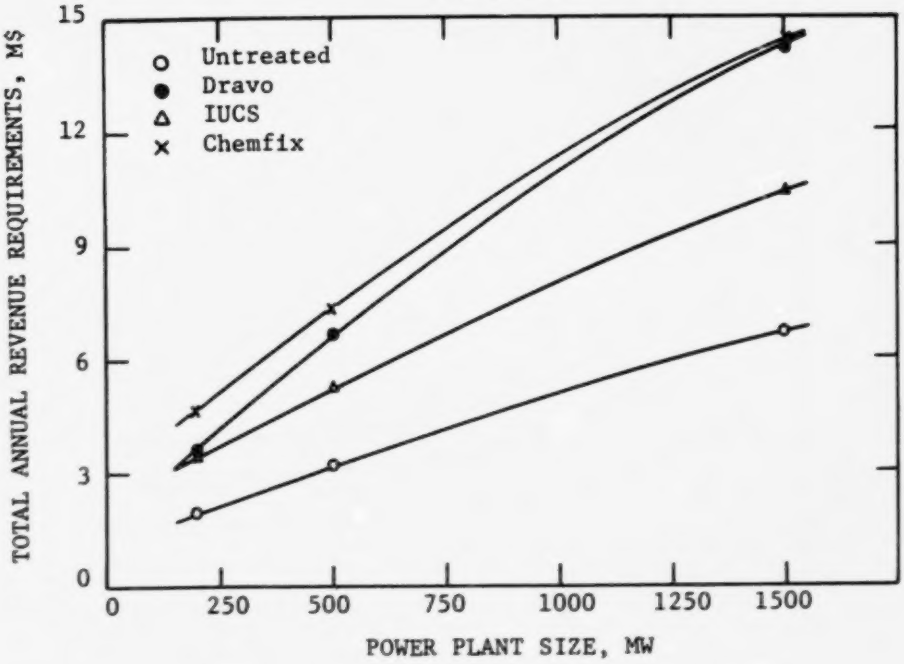

Figure 5. All processes. Effect of power plant size on total annual revenue requirements. New plants.

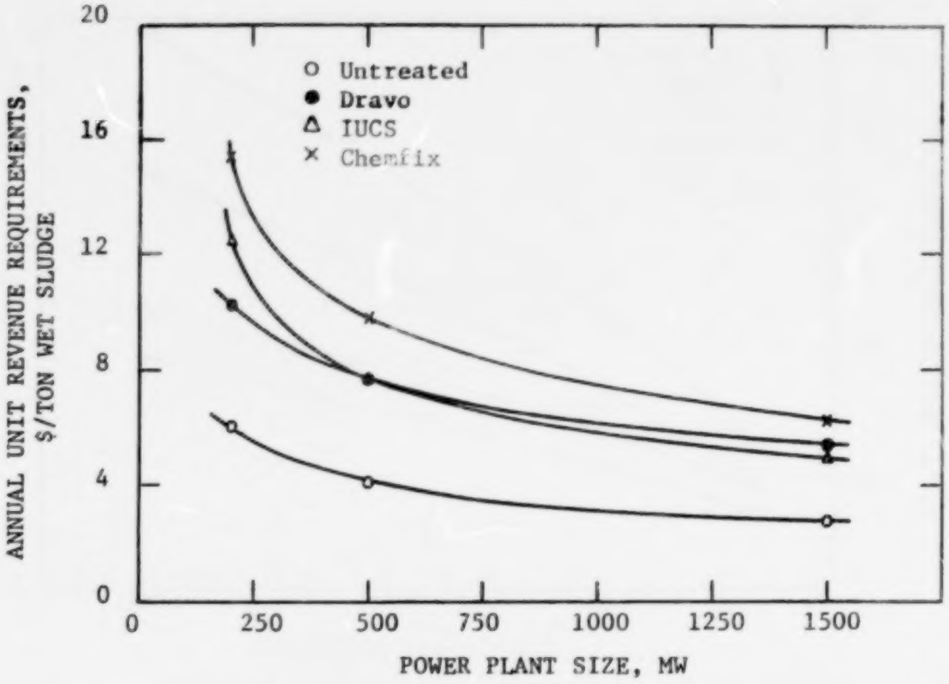

Figure 6. All processes. Effect of power plant size on annual unit revenue requirements. New plant.

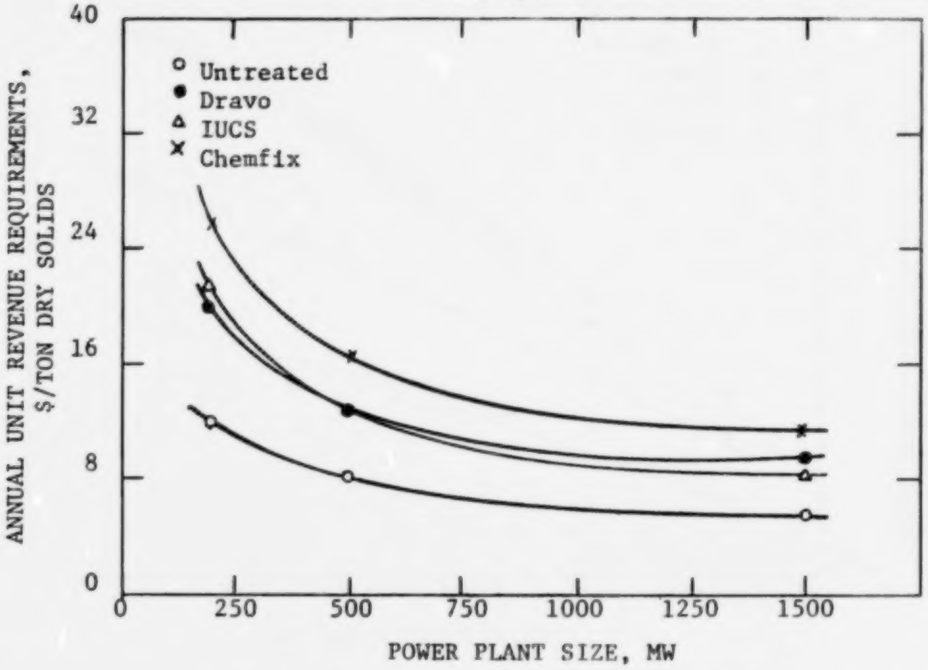

Figure 7. All processes. Effect of power plant size on annual unit revenue requirements. New plant.

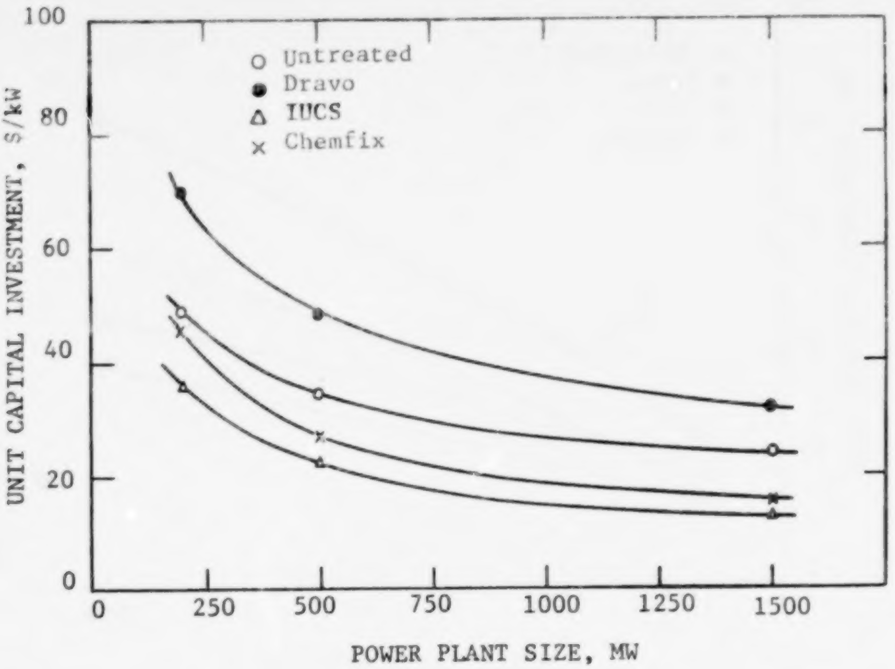

Figure 8. All processes. Effect of power plant size on unit capital investment. New plant.

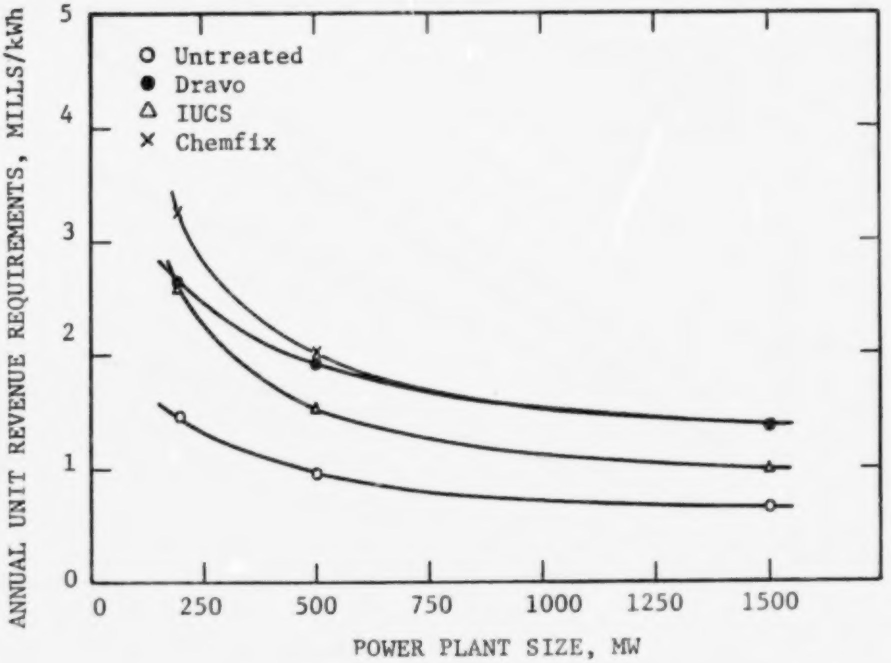

Figure 9. All processes. Effects of power plant size on annual unit revenue requirements. New plant.

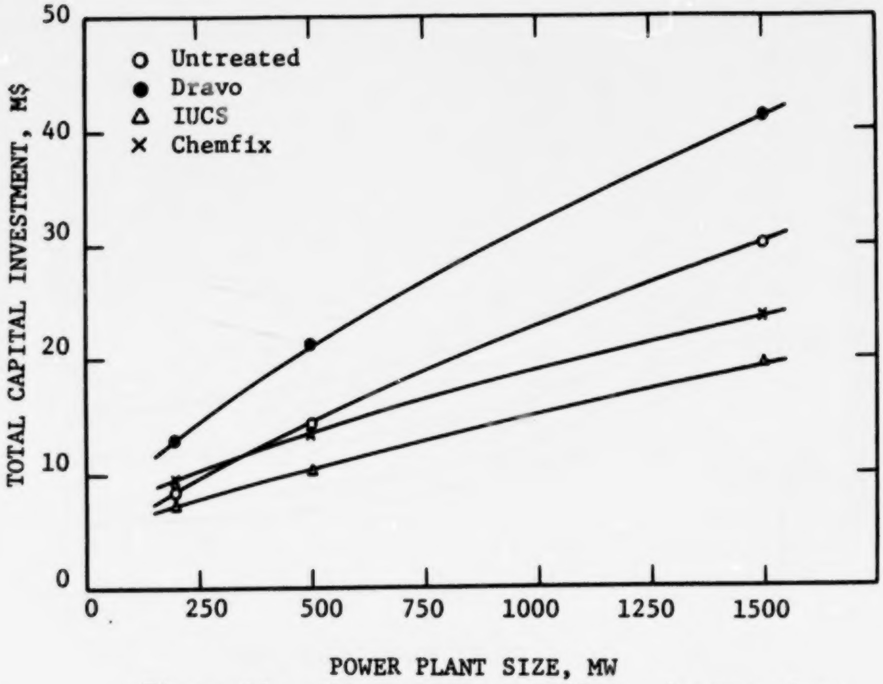

Figure 10. All processes. Effect of power plant size on total capital investment. Existing plant with 25 yr remaining life.

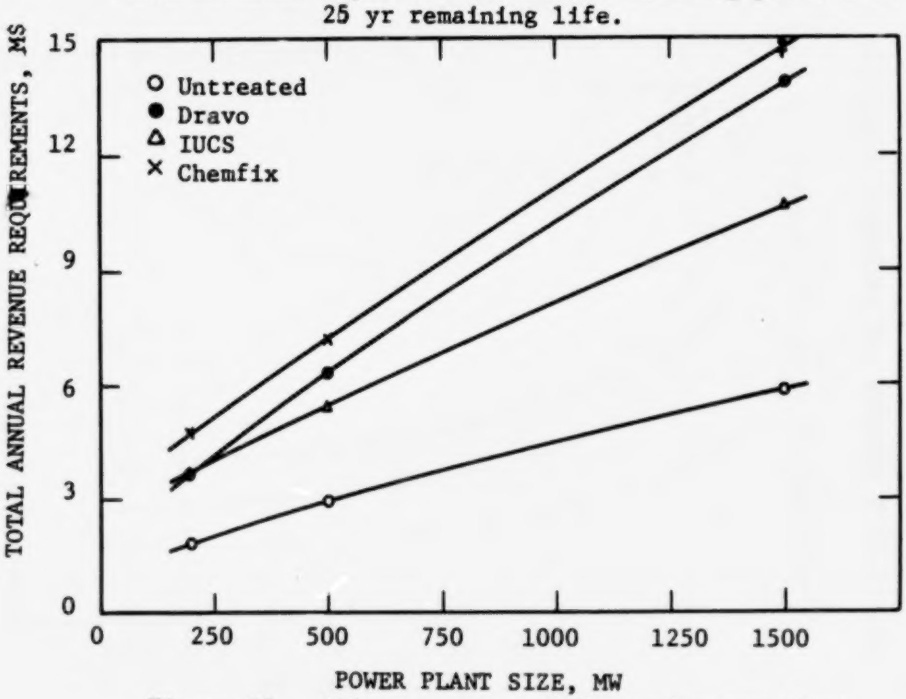

Figure 11. All processes. Effect of power plant size on total annual revenue requirements. Existing plant with 25 yr remaining life.

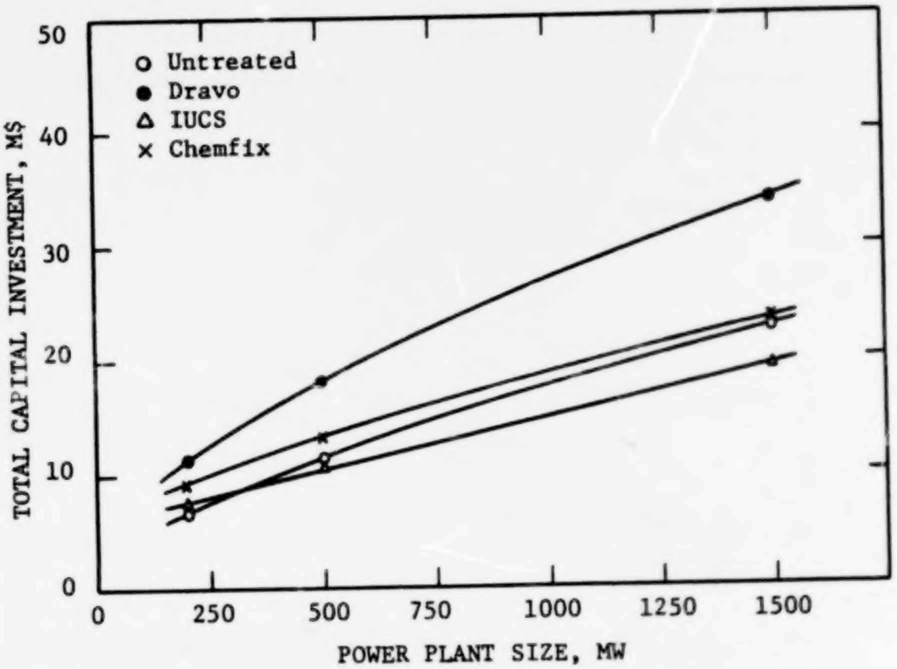

Figure 12. All processes. Effect of power plant size on total capital investment. Existing plant with 20 yr remaining life.

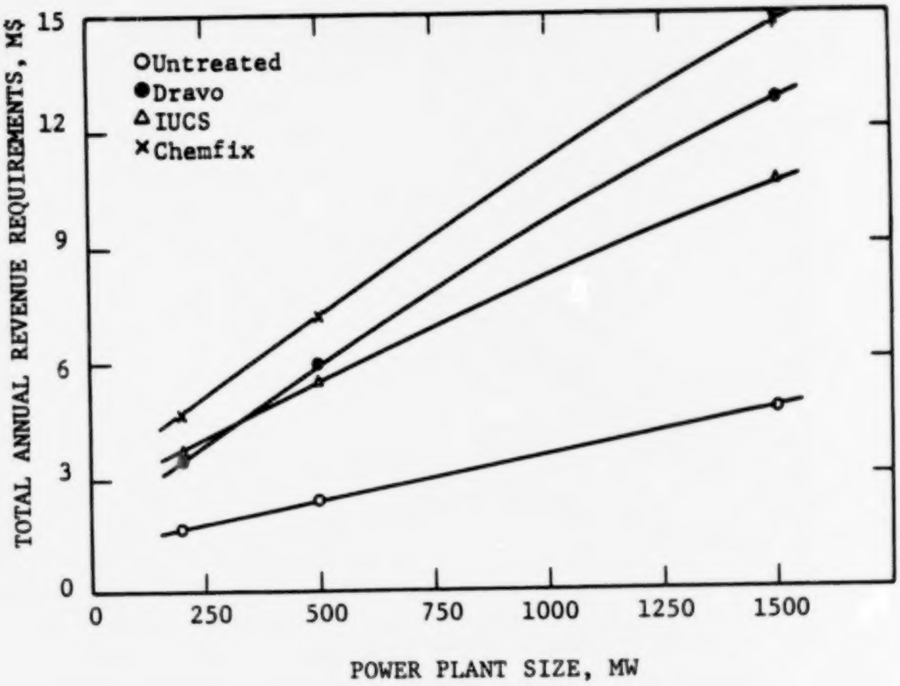

Figure 13. All processes. Effect of power plant size on total annual revenue requirements. Existing plant with 20 yr remaining life.

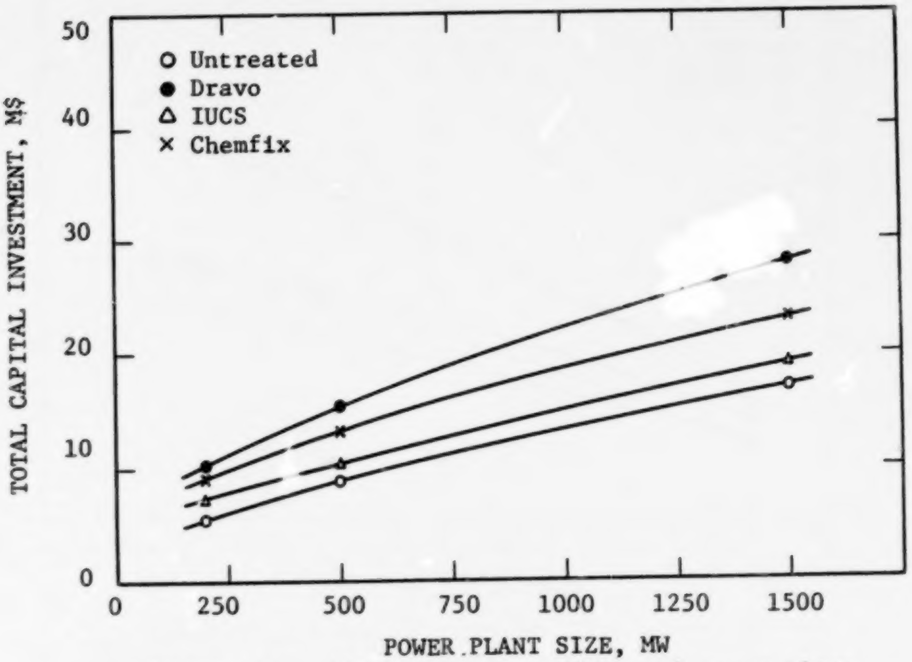

Figure 14. All processes. Effect of power plant size on total capital investment. Existing plant with 15 yr remaining life

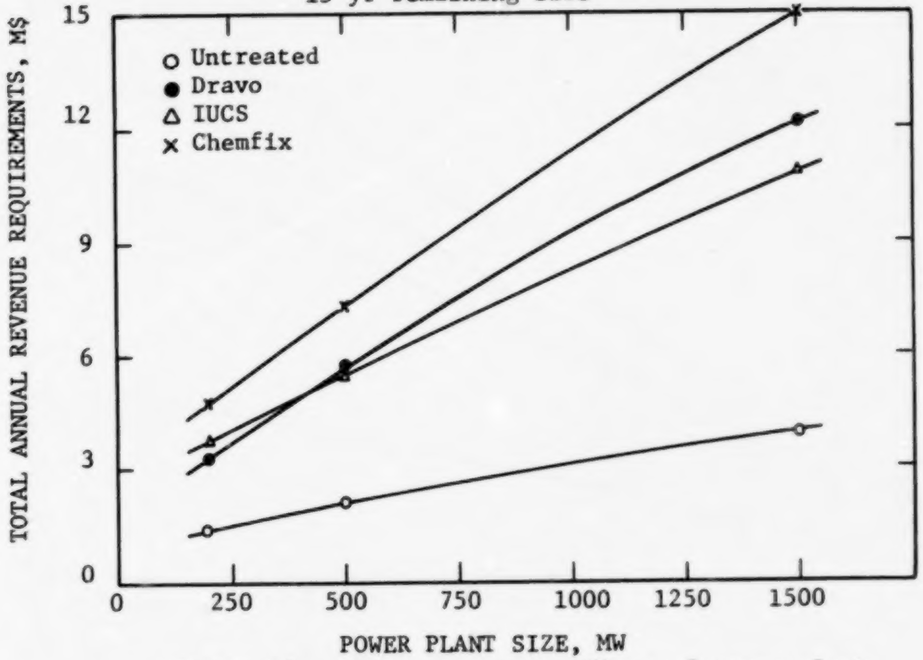

Figure 15. All processes. Effect of power plant size on total annual revenue requirements. Existing plant with 15 yr remaining life.

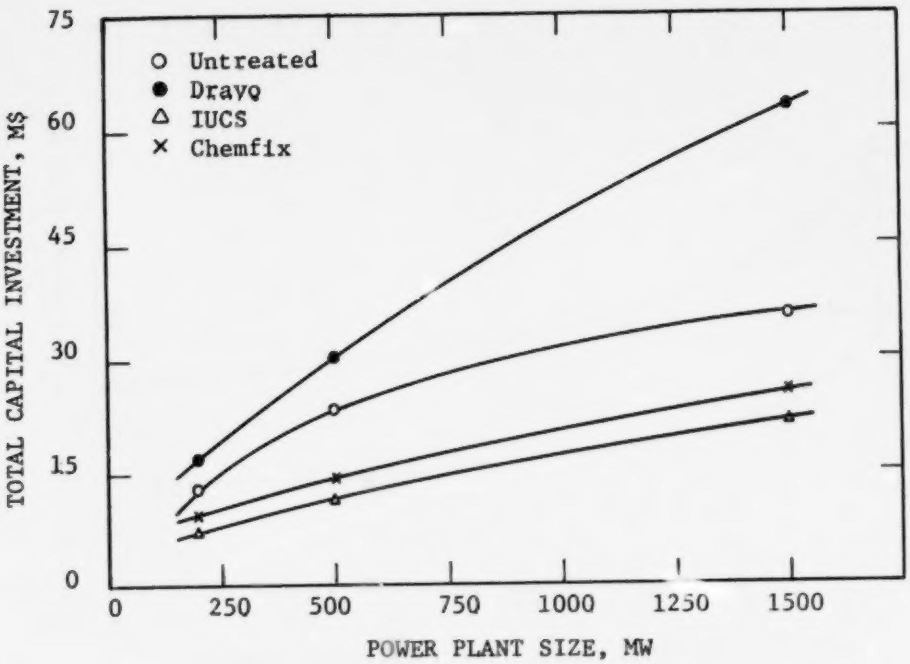

Figure 16. All processes. Effect of power plant size on total capital investment. New plant operating constant 7,000 hr/yr throughout its 30-yr life.

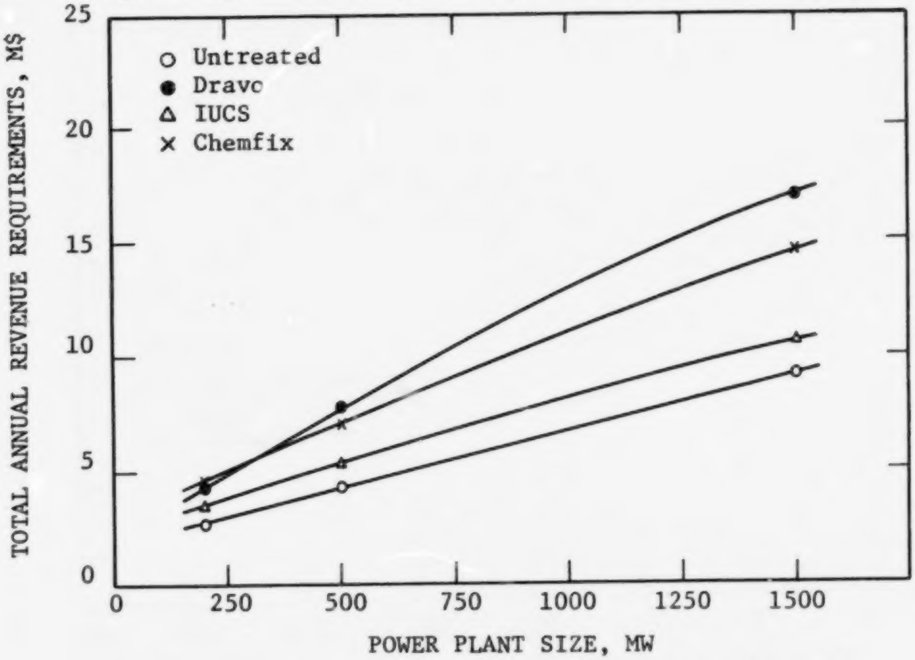

Figure 17. All processes. Effect of power plant size on total annual revenue requirements. New plant, operating constant 7,000 hr/yr throughout its 30-yr life.

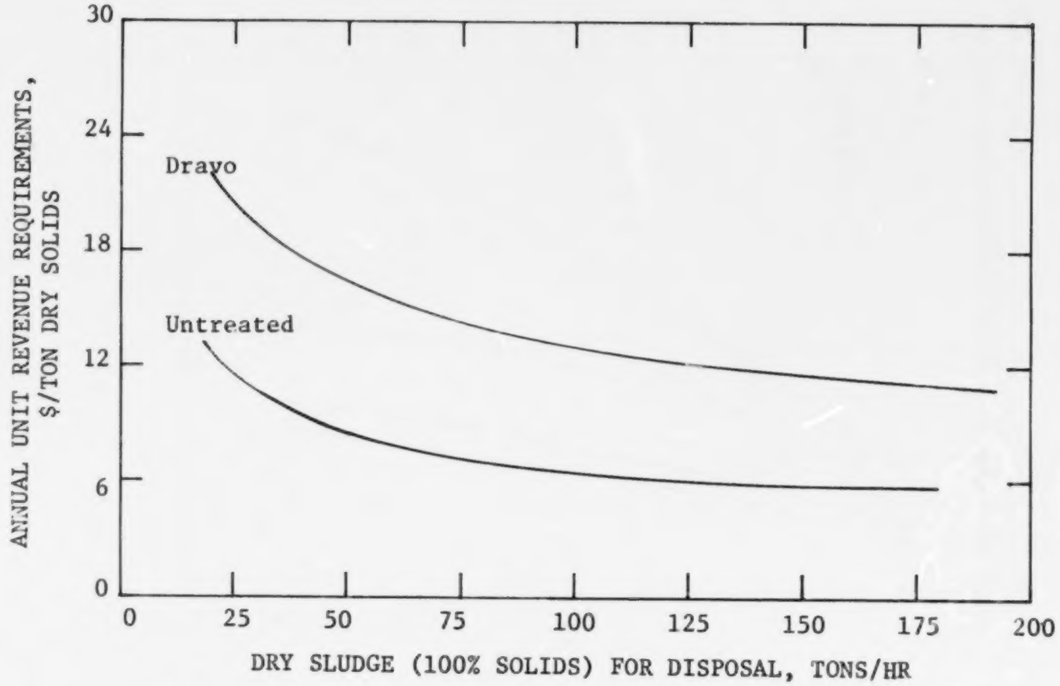

Figure 18. Untreated disposal and Dravo processes. Effect of sludge rate on annual unit revenue requirements.

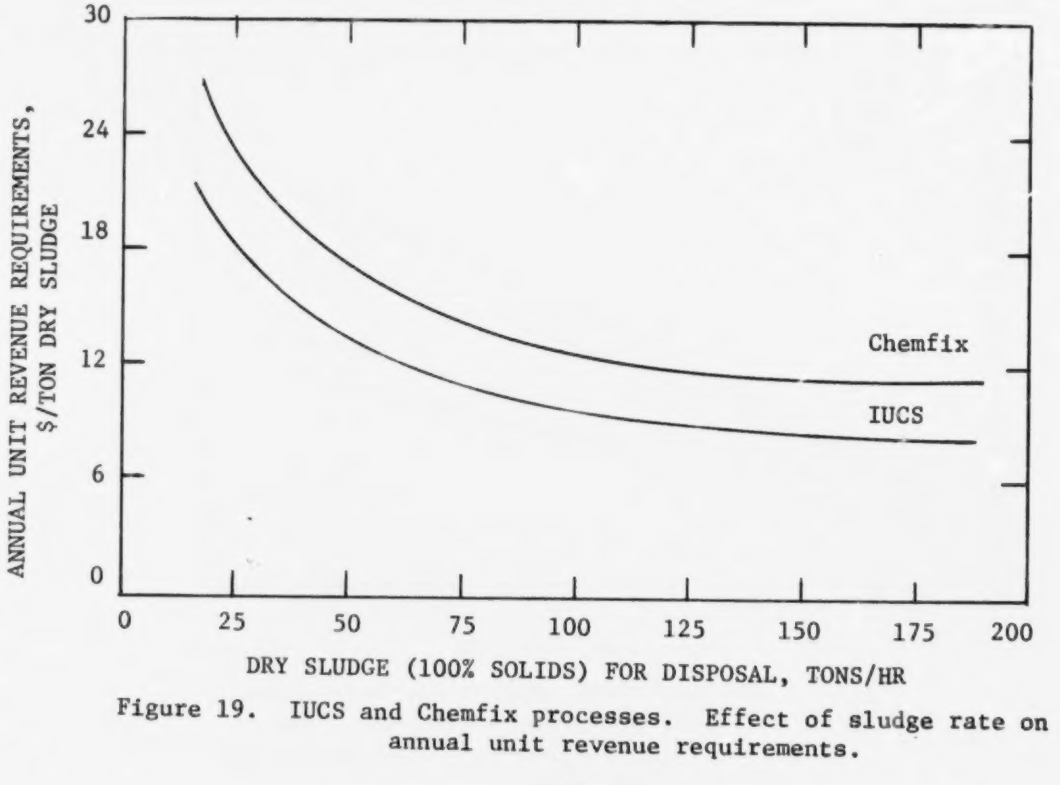

Figure 19. IUCS and Chemfix processes. Effect of sludge rate on annual unit revenue requirements.

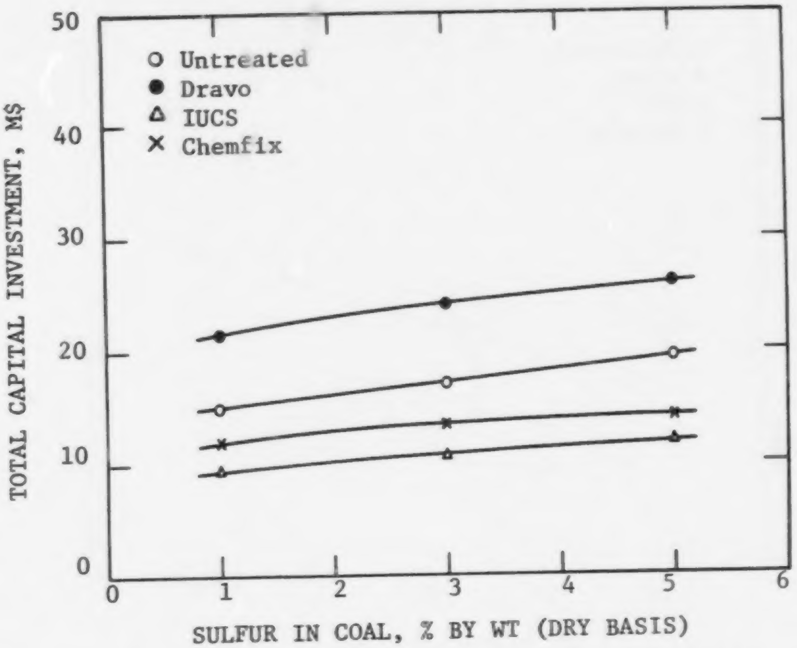

Figure 20. All processes. Effect of sulfur content of coal on total capital investment. New 500-MW plant.

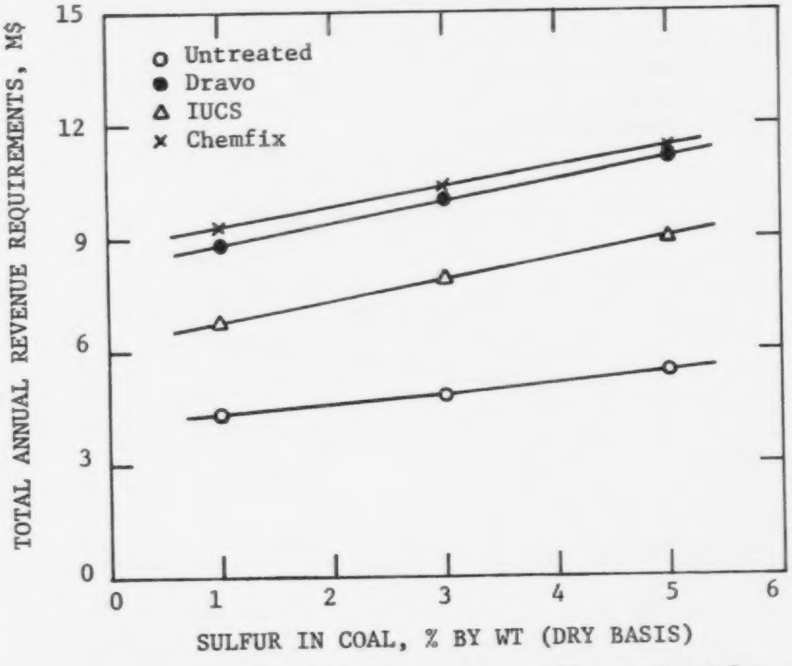

Figure 21. All processes. Effect of sulfur content of coal on total annual revenue requirements. New 500-MW plant.

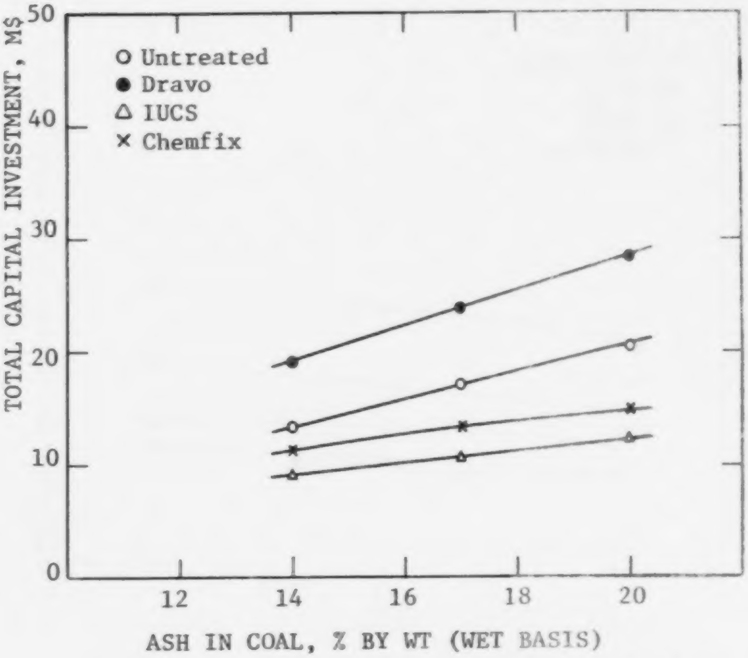

Figure 22. All processes. Effect of ash in coal on total capital investment. New 500-MW plant.

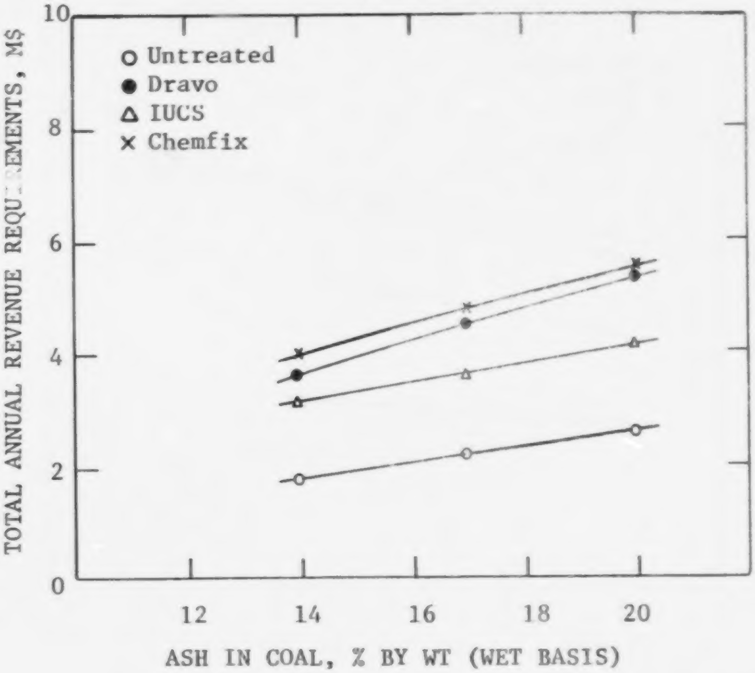

Figure 23. All processes. Effect of ash in coal on total annual revenue requirements. New 500-MW plant.

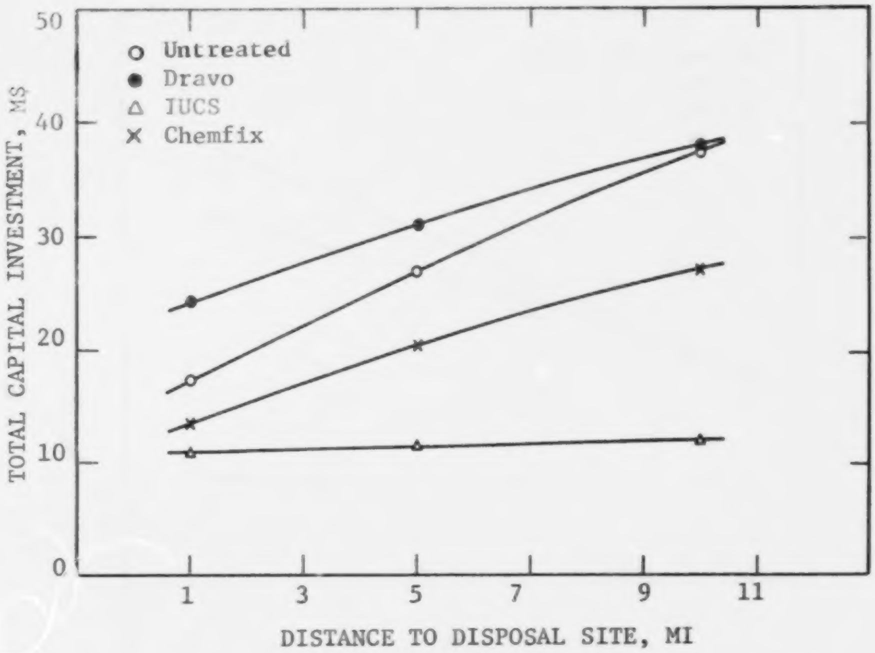

Figure 24. All processes. Effect of distance to disposal site on total capital investment. New 500-MW plant.

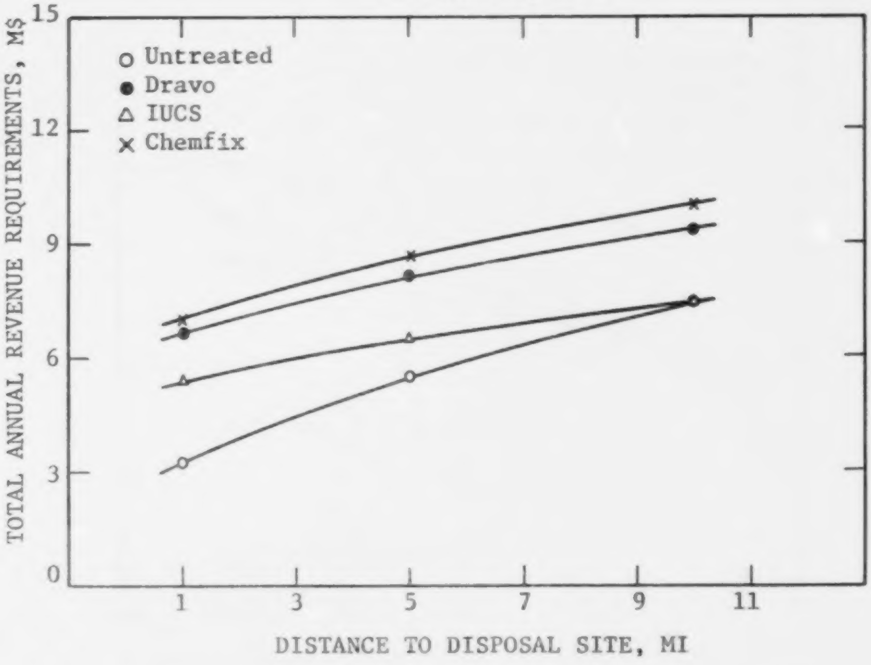

Figure 25. All processes. Effect of distance to disposal site on total annual revenue requirements. New 500-MW plant.

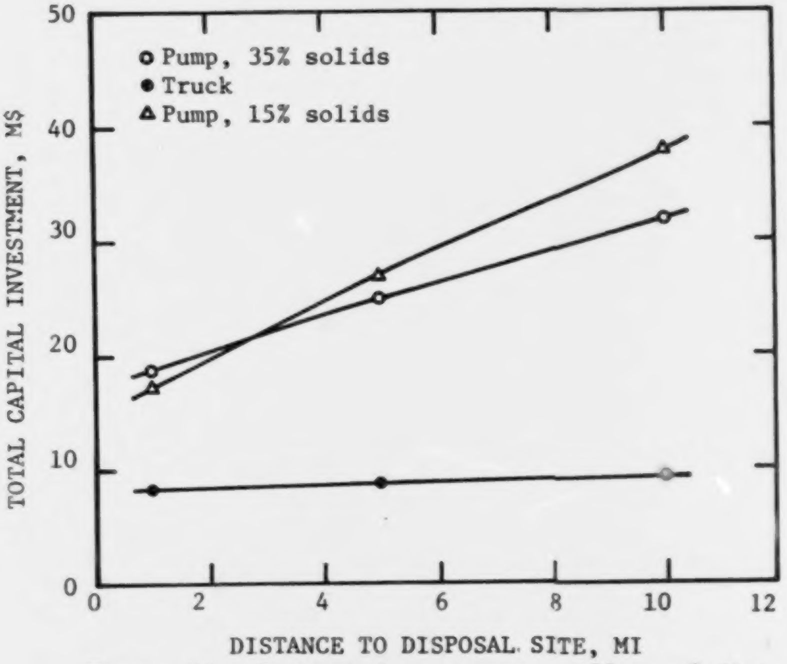

Figure 26. Untreated processes. Effect of distance to disposal site and mode of transport on total capital investment. New 500-MW plant.

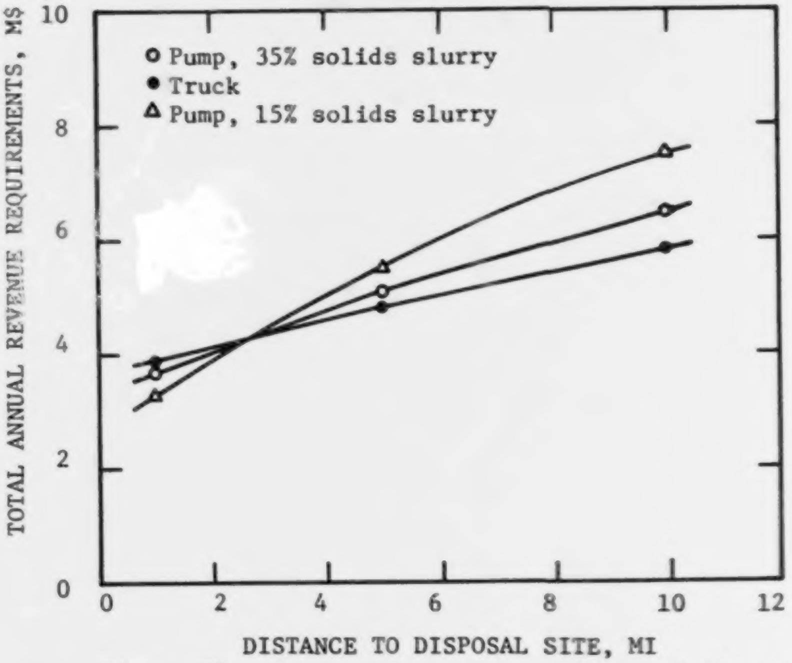

Figure 27. Untreated process. Effect of distance to disposal site and mode of transport on total annual revenue requirements. New 500-MW plant.

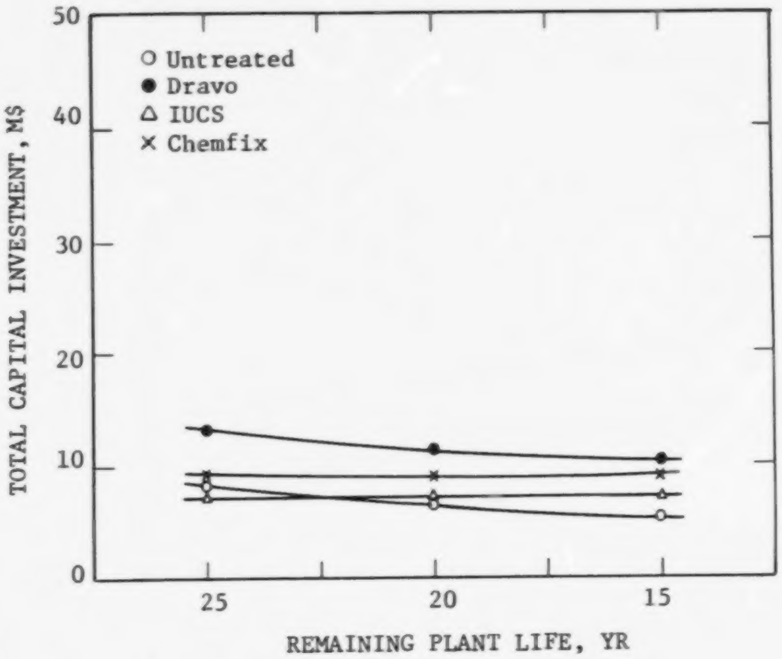

Figure 28. All processes. Effect of remaining plant life on total capital investment. 200-MW plant.

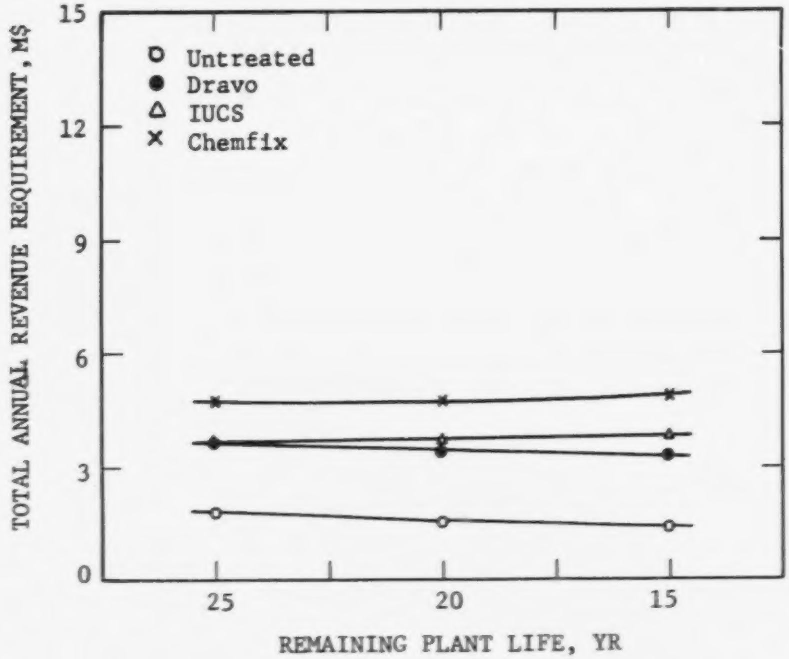

Figure 29. All processes. Effect of remaining plant life on total annual revenue requirement. 200-MW plant.

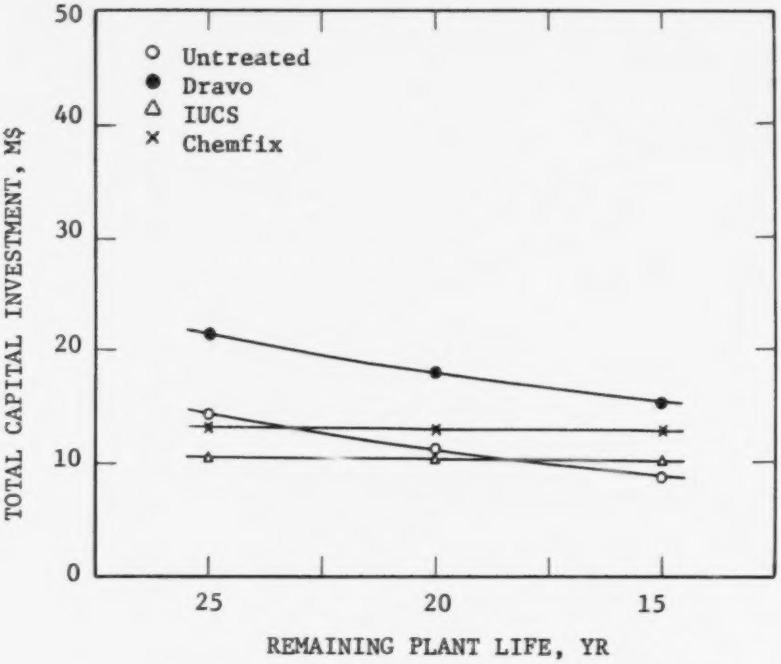

Figure 30. All processes. Effect of remaining plant life on total capital investment. 500-MW plant.

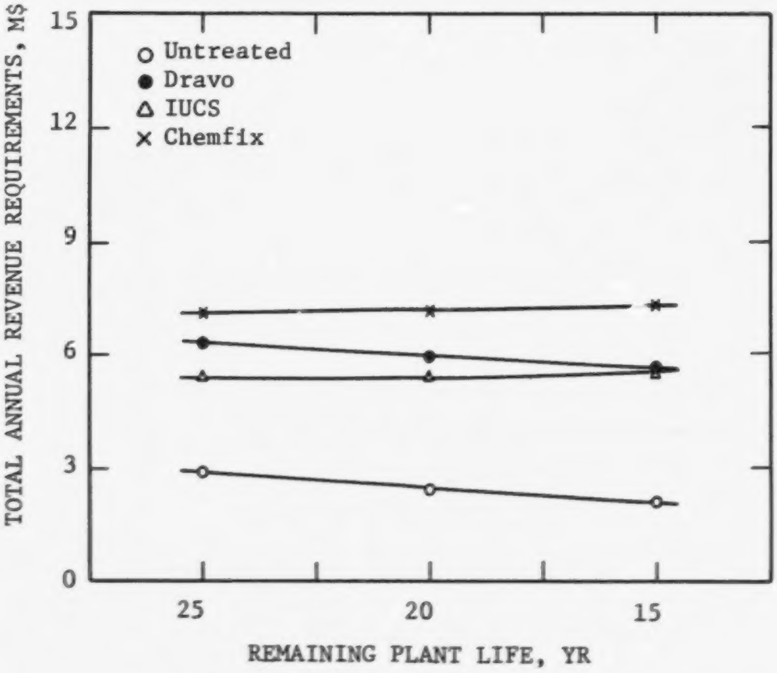

Figure 31. All processes. Effect of remaining plant life on total annual revenue requirement. 500-MW plant.

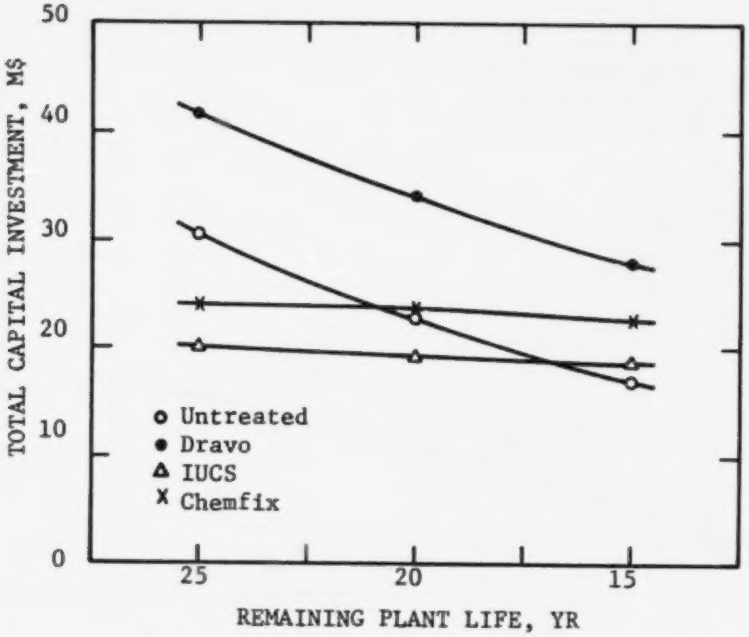

Figure 32. All processes. Effect of remaining plant life on total capital investment, 1500-MW plant.

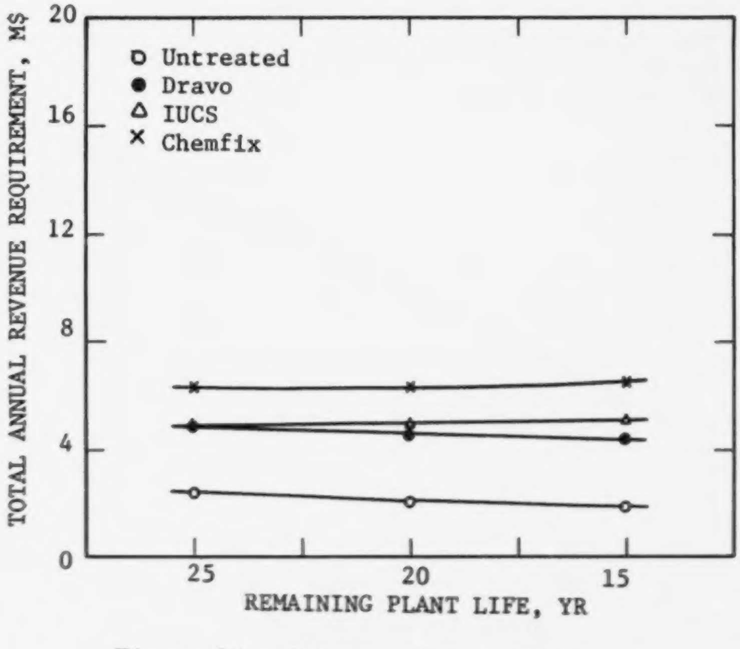

Figure 33. All processes. Effect of remaining plant life on total annual revenue requirement. 1500-MW plant.

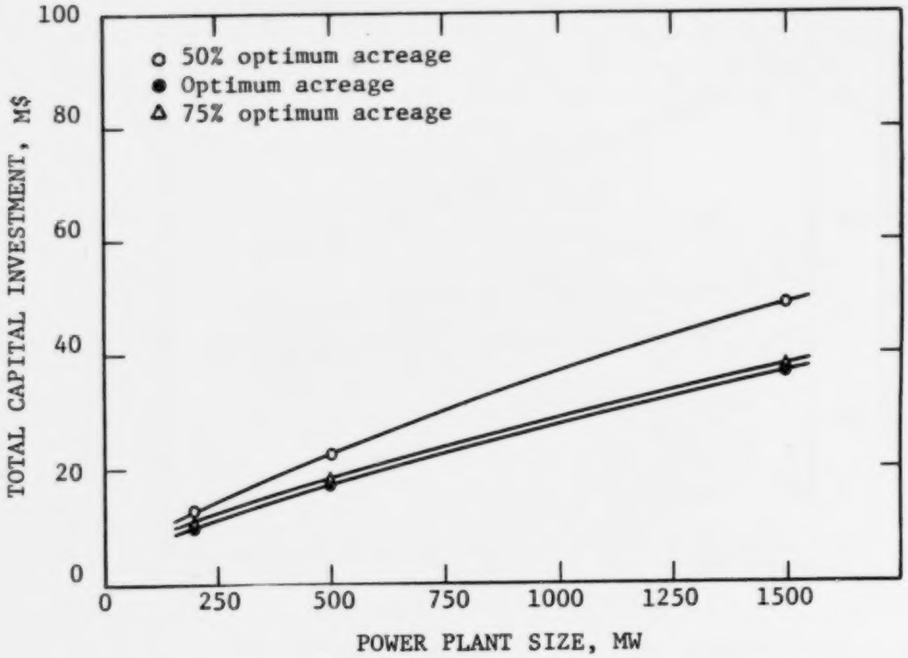

Figure 34. Untreated process. Effect of available pond acreage and power plant size on total capital investment.

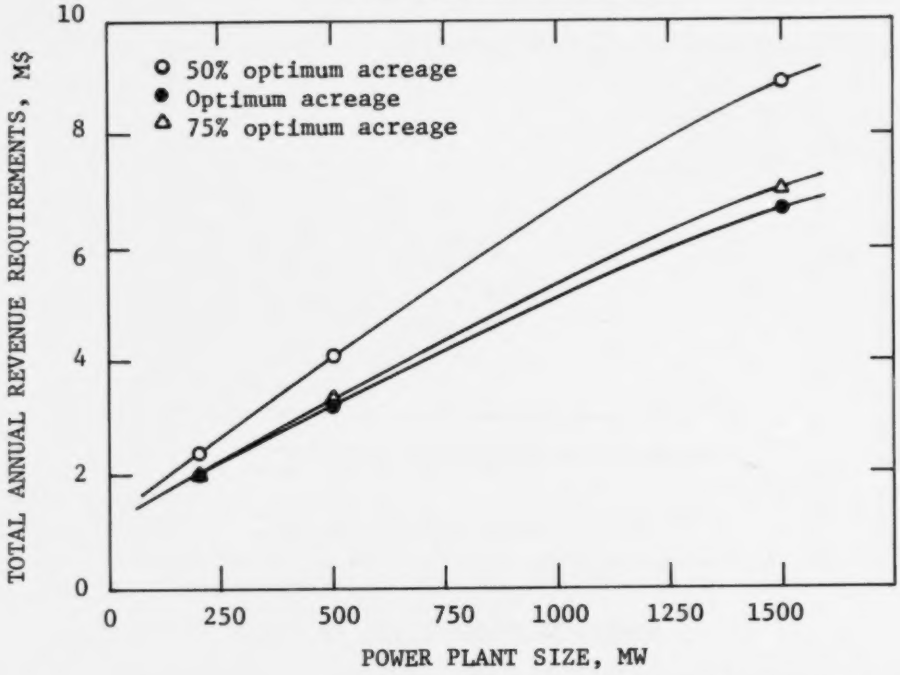

Figure 35. Untreated disposal. Effect of available pond acreage and power plant size on total annual revenue requirements.

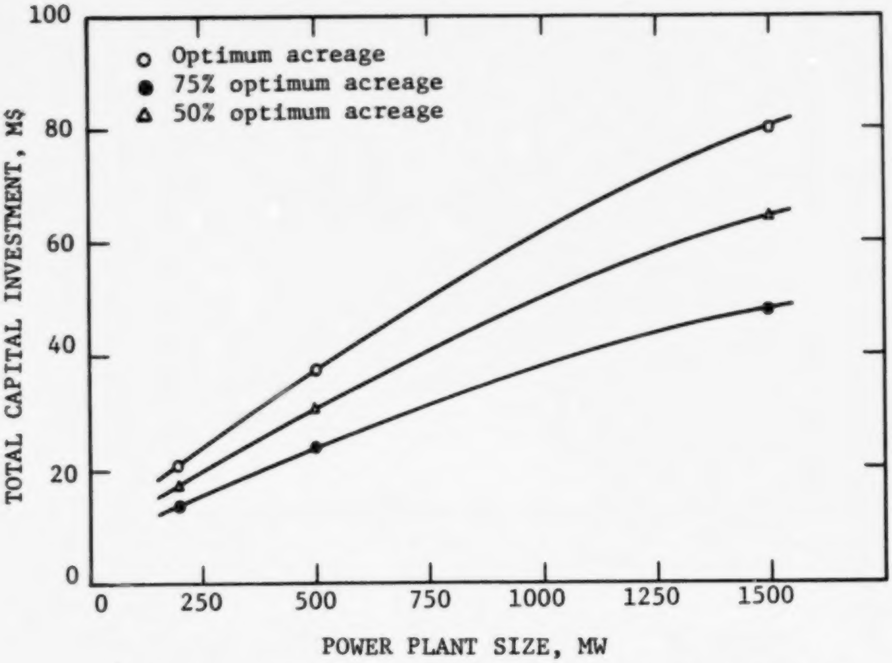

Figure 36. Dravo process. Effect of available pond acreage and power plant size on total capital investment.

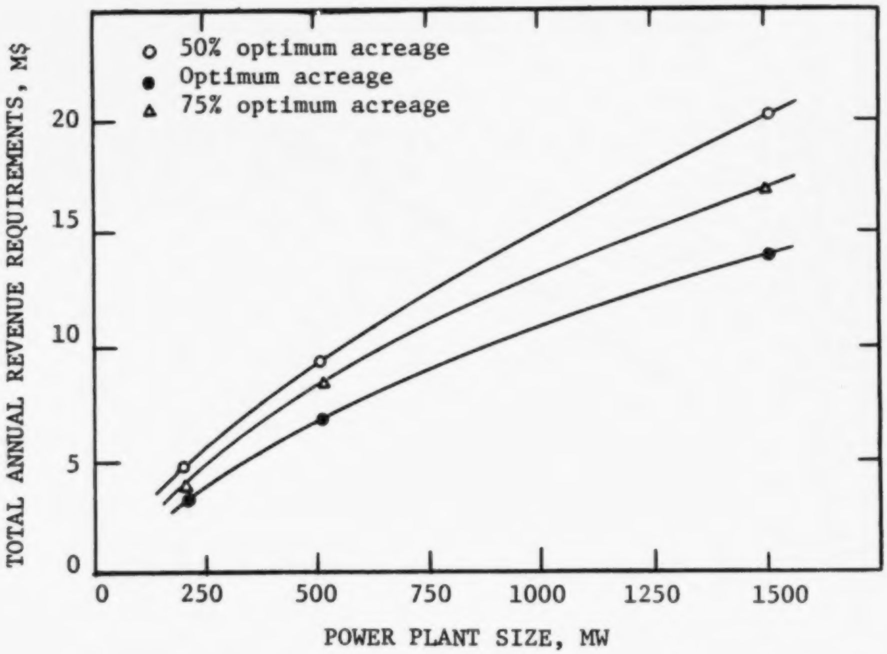

Figure 37. Dravo process. Effect of available pond acreage and power plant size on total annual revenue requirements.

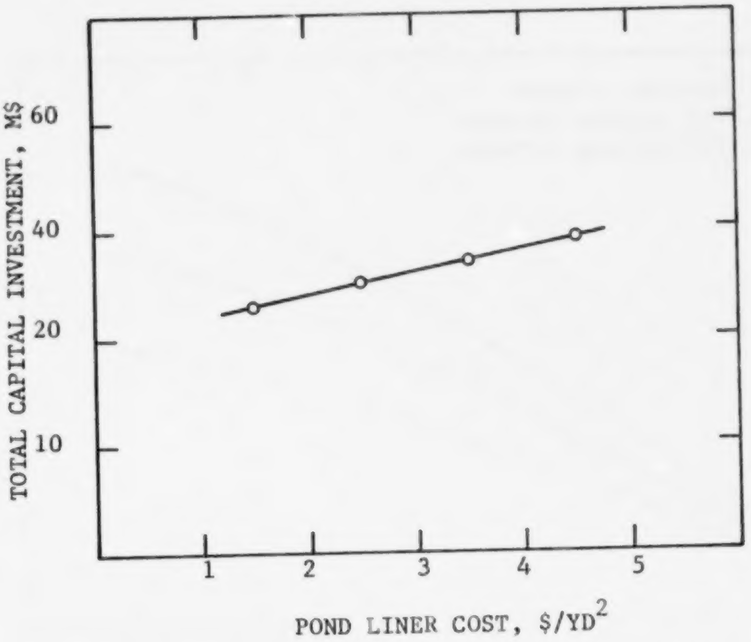

Figure 38. Untreated process. Effect of unit cost of pond liners on total capital investment. New 500-MW plant.

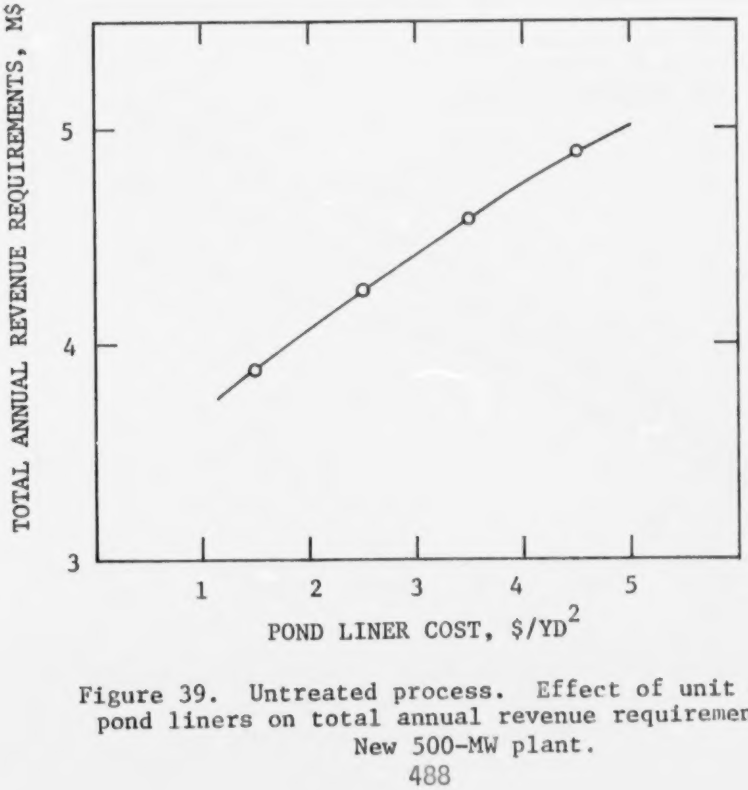

Figure 39. Untreated process. Effect of unit cost of pond liners on total annual revenue requirements. New 500-MW plant.

## TABLE 7. SUMMARY OF LIFETIME REVENUE REQUIREMENTS FOR ALL PROCESSES (ACTUAL AND DISCOUNTED CUMULATIVE TOTAL AND UNIT, MILLS/KWH) OVER THE LIFE OF THE POWER PLANT [a]

| Case[b] | Total actual lifetime revenue requirement, $ | Lifetime average unit revenue requirements, mills/kWh | Total present worth lifetime revenue requirement, $[c] | Levelized unit revenue requirements,[d] mills/kWh |
|---|---|---|---|---|
| Untreated | | | | |
| 200 MW | 58,750,000 | 2.30 | 20,204,800 | 2.03 |
| 500 MW | 97,757,800 | 1.53 | 33,612,100 | 1.35 |
| 1500 MW | 203,309,200 | 1.06 | 69,819,400 | 0.94 |
| Dravo | | | | |
| 200 MW | 94,392,200 | 3.70 | 33,368,200 | 3.36 |
| 500 MW | 175,764,900 | 2.76 | 62,052,600 | 2.50 |
| 1500 MW | 375,002,700 | 1.96 | 133,456,200 | 1.79 |
| IUCS | | | | |
| 200 MW | 89,013,000 | 3.49 | 30,584,100 | 3.08 |
| 500 MW | 131,224,200 | 2.06 | 45,381,700 | 1.83 |
| 1500 MW | 254,498,000 | 1.33 | 88,798,600 | 1.19 |
| Chemfix | | | | |
| 200 MW | 111,241,300 | 3.36 | 38,655,100 | 3.89 |
| 500 MW | 167,942,300 | 2.63 | 59,099,300 | 2.38 |
| 1500 MW | 333,190,900 | 1.74 | 119,154,500 | 1.60 |

a. Basis
Over previously defined power plant operating profile. 30-yr life: 7,000 hr for first 10 yr; 5,000 hr for next 5 yr; 3,500 hr for next 5 yr; 1,500 hr for next 10 yr.
Midwest plant location, 1980 operating costs.
Constant labor cost assumed over life of project.

b. New plants, coal analysis (wt %): 3.5% S (dry), 16% ash, flyash removed with $SO_2$ to meet NSPS.

c. Discounted at 10% to initial year.

d. Equivalent to discounted process cost over life of power plant.

## TABLE 8. SUMMARY OF LIFETIME REVENUE REQUIREMENTS FOR SYSTEMS OPERATING AT CONSTANT LOAD OF 7,000 HR/YR DURING 30-YR LIFE

## ACTUAL AND DISCOUNTED TOTAL AND UNIT INCREASE IN REVENUE REQUIREMENTS[a]

| Case[b] | Total actual lifetime revenue requirement, $ | Lifetime average unit revenue requirements, mills/kWh | Total present worth lifetime revenue requirement, $[c] | Levelized unit revenue requirements,[d] mills/kWh |
|---|---|---|---|---|
| Untreated | | | | |
| 200 MW | 80,584,600 | 1.92 | 26,228,200 | 2.26 |
| 500 MW | 137,899,200 | 1.31 | 45,197,300 | 1.56 |
| 1500 MW | 293,677,800 | 0.93 | 96,399,600 | 1.11 |
| Dravo | | | | |
| 200 MW | 129,537,700 | 3.08 | 41,066,500 | 3.53 |
| 500 MW | 243,352,900 | 2.32 | 76,570,300 | 2.64 |
| 1500 MW | 538,992,900 | 1.71 | 167,889,600 | 1.93 |
| IUCS | | | | |
| 200 MW | 111,398,500 | 2.65 | 33,019,700 | 2.84 |
| 500 MW | 167,635,400 | 1.60 | 49,563,800 | 1.80 |
| 1500 MW | 335,937,400 | 1.07 | 98,617,900 | 1.25 |
| Chemfix | | | | |
| 200 MW | 140,934,100 | 3.36 | 41,840,600 | 3.60 |
| 500 MW | 219,892,700 | 2.09 | 64,816,200 | 2.23 |
| 1500 MW | 457,926,200 | 1.45 | 133,464,500 | 1.53 |

[a] Basis
Midwest plant location, 1980 operating cost.
30-yr life at 7,000 hr/yr, 210,000 hr total operating time.

[b] New plants, coal analysis (wt %): 3.5% S (dry), 16% ash, flyash removed with $SO_2$ to meet NSPS.

[c] Discounted at 10% to initial year.

[d] Equivalent to discounted process cost over life of power plant.

## TABLE 9. SUMMARY OF LIFETIME REVENUE REQUIREMENTS FOR SYSTEMS OPERATING AT CONSTANT LOAD OF 5,000 HR/YR DURING 30-YR LIFE

### TOTAL AND UNIT REVENUE REQUIREMENTS OVER THE LIFE OF THE PLANT[a]

| Case[b] | Total actual lifetime revenue requirement, $ | Lifetime average unit revenue requirements, mills/kWh | Total present worth lifetime revenue requirement, $[c] | Levelized unit revenue requirements,[d] mills/kWh |
|---|---|---|---|---|
| Untreated | | | | |
| 200 MW | 68,635,900 | 2.29 | 22,269,300 | 2.68 |
| 500 MW | 113,972,700 | 1.52 | 37,296,900 | 1.80 |
| 1500 MW | 238,074,400 | 1.06 | 78,056,500 | 1.25 |
| Dravo | | | | |
| 200 MW | 111,652,500 | 3.72 | 35,498,100 | 4.28 |
| 500 MW | 202,043,900 | 2.69 | 63,826,800 | 3.08 |
| 1500 MW | 432,232,700 | 1.92 | 135,328,300 | 2.17 |
| IUCS | | | | |
| 200 MW | 105,897,500 | 3.53 | 31,497,700 | 3.79 |
| 500 MW | 154,682,700 | 2.06 | 45,980,100 | 2.22 |
| 1500 MW | 297,631,200 | 1.32 | 88,019,300 | 1.41 |
| Chemfix | | | | |
| 200 MW | 135,579,800 | 4.52 | 40,359,100 | 4.86 |
| 500 MW | 194,309,700 | 2.59 | 57,798,000 | 2.79 |
| 1500 MW | 382,117,300 | 1.70 | 112,489,900 | 1.81 |

---

a. Basis
   Midwest plant location, 1980 operating cost.
   30-yr life at 5,000 hr/yr, 150,000 hr total operating time.

b. New plants, coal analysis (wt %): 3.5% S (dry), 16% ash, flyash removed with $SO_2$ to meet NSPS.

c. Discounted at 10% to initial year.

d. Equivalent to discounted process cost over life of power plant.

## Land Requirements

The cost of land represents a significant portion of the total investment required for a sludge disposal system. As stated earlier, the cost of land was estimated to be $3500/acre. Land requirements for the four base case alternatives are as follows;

| Process | Acres | % of total capital investment |
|---|---|---|
| Untreated | 407 | 8.3 |
| Dravo | 414 | 6.0 |
| IUCS | 193 | 6.3 |
| Chemfix | 198 | 5.1 |

Land requirements for the case variations evaluated in this study varied from 21 to 1454 acres.

## CONCLUSIONS

Two categories of conclusions are discussed. The first is concerned with the economic comparisons of disposal process alternatives. The second category pertains to the effects of case variations for each of the disposal process alternatives.

### Economic Comparisons of Process Alternatives

The capital investment for an IUCS system is less than for the other alternatives evaluated for a new 500-MW plant (base case). The Dravo process for treatment and pond disposal was the most capital intensive alternative evaluated.

As the remaining life of the power plant is reduced, the untreated disposal option becomes the least expensive alternative for a 500-MW plant. The distance from the scrubber facilities to the disposal site has a large effect (29-117% increase) on capital investments for the alternatives using a disposal pond (untreated and Dravo).

Annual revenue requirements for a new 500-MW plant (base case) disposal system are lowest for the untreated disposal alternative. The Chemfix process generally has the highest annual revenue requirements.

### Effects of Case Variations for Each Alternative

Table 10 shows the effects on total capital investment and annual revenue requirement by case variations for each disposal alternate.

Untreated disposal. The major cost variable for these cases is the disposal pond. Any case variation resulting in a change in the quantity of material for disposal results in a similar change in capital investment. Additional dewatering of the sludge before disposal (assuming suitable for truck transport), results in a reduction (50%) in capital investment. Revenue requirements and capital investments are affected considerably (21-129% increase) by the distance to the disposal site.

# TABLE 10. EFFECTS ON TOTAL CAPITAL INVESTMENT AND ANNUAL REVENUE REQUIREMENT BY CASE VARIATIONS FOR ALL PROCESSES

| | Degree of change from base case[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Capital investment | | | | Revenue requirements | | | |
| Case variations | Untreated | Dravo | IUCS | Chemfix | Untreated | Dravo | IUCS | Chemfix |
| Plant size | Large | Large | Large | Large | Large | Large | Large | Large |
| Remaining plant life | Large | Moderate | Slight | Slight | Moderate | Small | Slight | Slight |
| Ash in coal | Small | Small | Small | Small | Small | Small | Small | Small |
| Sulfur in coal | Moderate | Small | Small | Small | Small | Moderate | Small | Small |
| No flyash in sludge | Moderate | Small | Slight | Moderate | Moderate | Moderate | Small | Moderate |
| Distance to disposal | Large | Large | Small | Large | Large | Large | Large | Large |
| Fixation additive rate | - | Slight | Slight | Small | - | Small | Slight | Large |
| Limestone vs lime scrubbing process | Slight | Small | Slight | Slight | Slight | Slight | Slight | Small |
| Thickened sludge | Small | - | - | - | Small | - | - | - |
| Thickened sludge and distance to disposal site | Large | - | - | - | Large | - | - | - |
| Filtered sludge | Large | - | - | - | Small | - | - | - |
| Filtered sludge and distance to disposal site | Large | - | - | - | Large | - | - | - |
| Constraint of available pond acreage | Moderate | - | - | - | Moderate | - | - | - |
| Pond lining | Large | - | - | - | Large | - | - | - |
| Truck to disposal | - | - | - | Small | - | - | - | Slight |
| Intermediate ponding and truck to landfill | - | Large | - | - | - | Slight | - | - |
| Settled density in pond | Small | Large | - | - | Small | Large | - | - |

[a] An arbitrary scale is established with the following rating criteria being applied.
Slight: less than ±10% change from the base case
Small: from ±10% to ±20%
Moderate: from greater than ±20% to ±40%
Large: greater than ± 40%

Dravo process. Capital investments are affected by the size of the disposal pond required as were the untreated disposal cases. The Dravo process for intermediate ponding, truck transport, and landfill disposal requires 47% less capital investment than the base case (pond disposal). Revenue requirements (per unit) are affected most by the distance to the disposal site.

IUCS process. This process requires flyash for stabilization and the case variations for ESP flyash collection have higher capital investments than the base case. This increase is due to the cost of equipment for handling and storage of flyash to be put back into the sludge. Revenue requirements are affected considerably by the distance to the disposal site (+40% increase), and the quantity of sludge for disposal (up to 208% increase).

Chemfix process. Capital investments and revenue requirements are also greatly increased (25-100%) by the distance to the disposal site (pipe lines are used for transport of sludge containing 35% solids to the treatment-disposal site) for this process. Case variations for increased fixation additive rates have significantly higher capital investments and revenue requirements.

## Additional Work and Recommendations

Another TVA-EPA study is underway, using the same premises as this study, to evaluate two additional sludge disposal alternatives: (1) gypsum produced by the lime or limestone system with forced oxidation, and (2) untreated sludge that is physically stabilized by dewatering and blending with dry flyash. The study is scheduled for completion in early 1978. Studies are needed to evaluate new disposal technology, to update the processes already evaluated, and to reflect the latest environmental requirements. Dravo now offers a landfill disposal process that should be evaluated. Alternatives such as mine disposal should be investigated further to determine if an economic evaluation is warranted.

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# FLUE GAS DESULFURIZATION WASTE DISPOSAL FIELD STUDY AT THE SHAWNEE POWER STATION

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## ABSTRACT

This paper summarizes and assesses the results obtained since the inception in 1974 of the U.S. Environmental Protection Agency Flue Gas Desulfurization Waste Disposal Field Evaluation Project at the Tennessee Valley Authority Shawnee electric generating plant, Paducah, Kentucky. Eight disposal ponds containing lime or limestone flue gas scrubbing sludges are being monitored. The wastes, or sludges, were produced by two 10-MW equivalent prototype scrubbers: a venturi spray tower and a turbulent contact absorber. Five of the ponds contain untreated sludges, and each of the other three contains sludge that was chemically treated by one of three processors: Chemfix, Dravo, and IU Conversion Systems.

Variations in the concentrations of major constituents and trace elements in the leachate, supernate, and groundwaters as a function of time are discussed for each of the ponds. Physical and engineering properties of cores taken from the chemically treated ponds are presented, and the physical and chemical characteristics of untreated sludges placed in ponds having underdrainage systems are discussed. The potential environmental impacts, safe disposal methods, and the economics for operational sites are also discussed.

## CONVERSION TABLE

| British | Metric |
|---|---|
| 1 acre | 4047 square meters |
| 1 British thermal unit per pound | 2.235 Joules per gram |
| 1 foot | 0.3048 meter |
| 1 cubic foot | 28.316 liters |
| 1 inch | 2.54 centimeters |
| 1 gallon (U.S.) | 3.785 liters |
| 1 pound | 0.454 kilogram |
| 1 mile | 1.609 kilometers |
| 1 ton (short) | 0.9072 metric tons |
| 1 ton per square foot | 9765 kilograms per square meter |
| 1 part per million | 1 milligram per liter (equivalent) |
| 1 pound per square inch | 0.0703 kilogram per square centimeter |
| 1 cubic yard | 0.7641 cubic meter |

## SECTION 1. INTRODUCTION

The flue gas desulfurization (FGD) waste disposal field evaluation project at the Tennessee Valley Authority (TVA) Shawnee Steam Plant in Paducah, Kentucky, was initiated in September 1974. The project, which is being conducted by the Environmental Protection Agency (EPA) Industrial Environmental Research Laboratory (IERL), Research Triangle Park (RTP), North Carolina, was planned and is being coordinated and evaluated by The Aerospace Corporation. Site construction and field and analytical support are provided by TVA. Coordination with the site scrubber test program is provided by the Bechtel Corporation, which conducts the scrubber test program. The purpose of this project is to assess the effects of various disposal techniques and field operating procedures, involving FGD sludge, on the environmental quality of the disposal site.

The objectives of this project are as follows:

a. Evaluate current disposal techniques under critical field operating conditions.

b. Evaluate the environmental acceptability of current disposal technology through periodic sampling, analysis, and assessment of water, soil, and sludge cores.

c. Develop engineering cost estimates for alternative disposal methods on an operational basis.

Currently, eight disposal ponds are under evaluation, two of which were activated in 1977. A summary of the sludge types being used and the input conditions are listed in Table 1. Five ponds contain untreated sludge, and the remaining ponds contain sludges treated by three different chemical processors. The treatment processes and estimates of the respective costs have been reported.[1,2] With the exception of Pond H, which is filled with ash-free oxidized sulfite (gypsum), all ponded sludges contain approximately 40-percent fly ash on a dry weight basis, the fly ash either being present during scrubbing or added during disposal.

This paper provides a general description of the test site, characteristics of untreated and chemically treated sludges and their leachates, interim results from this project, a preliminary assessment, disposal alternatives, and disposal cost estimates.

## SECTION 2. PROJECT DESCRIPTION

The ponds were filled between 7 October 1974 and 30 September 1977 and will continue to be evaluated at least through March 1978. All ponds are monitored for leachate, supernate, groundwater quality, and characteristics of the soil on the pond bottom. Also, sludge cores from the ponds containing chemically treated material are evaluated for chemical and physical characteristics.

Initially, this project involved five impoundments, each occupying approximately 0.1 acre and filled to a depth of 3 feet.[1,2] Two of these ponds contained untreated sludge, and three contained sludge that had been chemically

## Table 1. SHAWNEE POND FILL DATA

| Pond | Fill Date | Scrubber Type | Sludge | | Solids Content, wt% | Treatment Contractor |
|---|---|---|---|---|---|---|
| | | | Absorbent | Source | | |
| A | 10/8/74 | Venturi and spray tower | Lime | Filter | 46 | Untreated |
| A1[a] | 5/10/76 | Venturi and spray tower | Lime | Filter | 46 | Untreated |
| B | 4/15/75 | Turbulent contact absorber | Limestone | Clarifier underflow | 38[b] | Dravo |
| C | 4/23/75 | Venturi and spray tower | Lime | Centrifuge | 55[b] | IU Conversion Systems |
| D | 2/5/75 | Turbulent contact absorber | Limestone | Clarifier underflow | 38 | Untreated |
| E | 12/7/74 | Turbulent contact absorber | Limestone | Clarifier underflow | 38[b] | Chemfix |
| F | 2/3/77 | Turbulent contact absorber | Limestone | Clarifier underflow | 47 | Untreated |
| G | 10/5/76 | Venturi and spray tower | Lime | Centrifuge | 47 | Untreated |
| H | 9/2/77 | Venturi and spray tower | Limestone (gypsum) | Clarifier underflow | 33 | Untreated |
| | 9/30/77 | Venturi and spray tower | Limestone (gypsum) | Filter | 86 | Untreated |

[a] Transferred from Pond A.

[b] Prior to chemical treatment.

treated. During 1976 and 1977, the program was expanded to provide for three additional ponds to be filled with ash-free lime sludge, ash-free limestone sludge, and oxidized sulfite (gypsum) sludge, all of which were provided with an underdrainage system. All three sites were constructed, and the pond designated for ash-free lime sludge was filled in October 1976. The remaining two sites were filled in February and September 1977.

The disposal ponds were filled with sludges representing a cross section of scrubber effluent conditions. The five ponds filled with untreated sludge (A1, D, F, G, and H), shown in Figures 1 through 5, were selected for evaluation of both lime and limestone scrubbing waste disposal including sludge containing fly ash, ash-free sludge to which fly ash was added during ponding, gypsum, drained and undrained ponds, and variations in the degree of sludge dewatering. Ponds A1 and D are control ponds; F, G, and H are for evaluation. The materials used in the evaluation of chemical treatment were representative of various disposal operating conditions. Pond B (Figure 6) was filled with limestone sludge clarifier underflow, chemically treated by the Dravo Corporation, and placed in the pond under conditions approximating disposal under water behind a dam. Pond C (Figure 7), was filled with lime sludge that had been dewatered by centrifugation, chemically treated by IU Conversion Systems, Inc., and stored in a pond under conditions representing a low spot in a landfill in which rainwater is contained. Pond E (Figure 8) was filled with limestone sludge clarifier underflow, chemically treated by Chemfix, and placed in the pond under conditions similar to those for Pond C. Details of the pond filling operations for Ponds A through E are described in the initial report on this project including processor recommendations on additive quantities for each of the three chemical treatment processes.[1] Descriptions of the three ponds filled during 1976 and 1977, i.e., F, G, and H, are presented here in the chronological order in which they were filled.

## 2.1 LIME SLUDGE WITH UNDERDRAINAGE (POND G)

Pond G was filled during the period of 30 September through 5 October 1976, with layered sludge and fly ash. The sludge was obtained from the Chemico venturi and spray tower during an ash-free scrubbing run, with lime as the absorbent. Total ash removed upstream of the scrubber was approximately 40 weight percent of the sludge solids. The sludge was dewatered by centrifuging, mixed with one-half the fly ash to 47-percent solids, and loaded into rotary mix trucks for transport to the pond. This material was layered into the pond with the remaining fly ash. The pond is 40 × 40 feet at the top of the berms, has 2:1 slopes, and is equipped with an underdrain system consisting of 4-in.-diam PVC perforated pipes covered with pea gravel and a 1-foot sand layer.

The underdrain water is collected by gravity flow in a 100-gallon tank and pumped to the surface automatically by a float-actuated pump. The pond was filled to a depth of 4 feet, which represents a total volume of approximately 85 cu yd. Pond G will be used to evaluate the environmental acceptability of ash-free lime sludge remixed with fly ash and will also be tested for bearing-strength qualities as a landfill material.

## 2.2 LIMESTONE SLUDGE WITH UNDERDRAINAGE (POND F)

Pond F was filled during the period of 28 January through 3 February 1977 with ash-free limestone sludge remixed with fly ash. The sludge was obtained from the Universal Oil Products (UOP) turbulent contact absorber (TCA) during an ash-free scrubbing run, with limestone as the absorbent. Clarifier

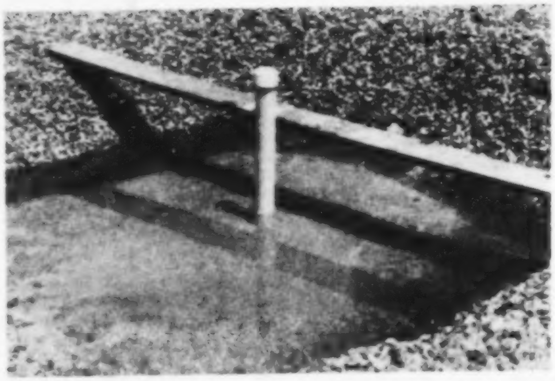


Figure 1. Pond A1: lime, filter cake

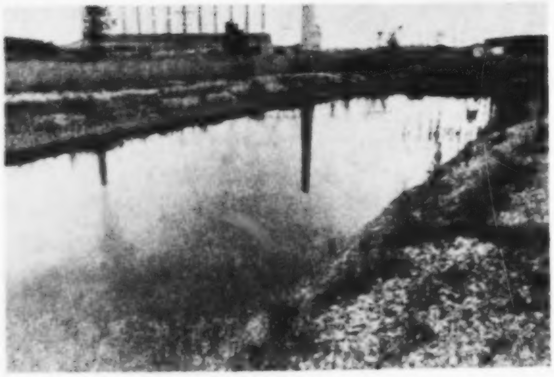
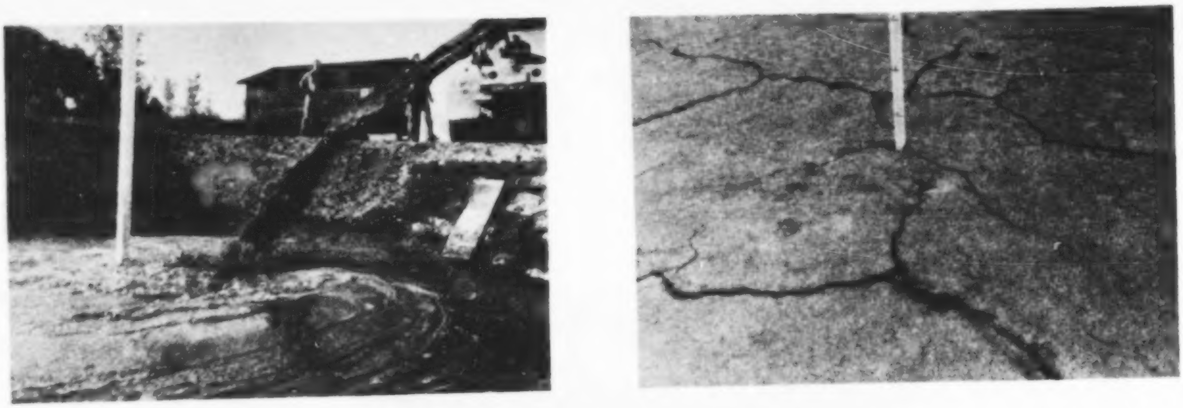


Figure 2. Pond D: limestone, clarifier underflow



a. During filling

b. Typical surface condition

Figure 3. Pond F (underdrained): limestone, clarifier underflow

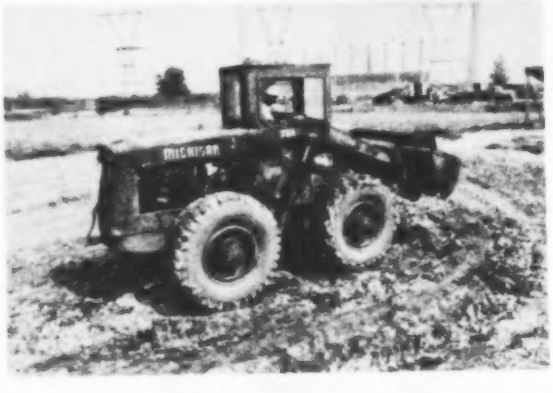


Figure 4. Pond G (underdrained): lime, centrifuge cake

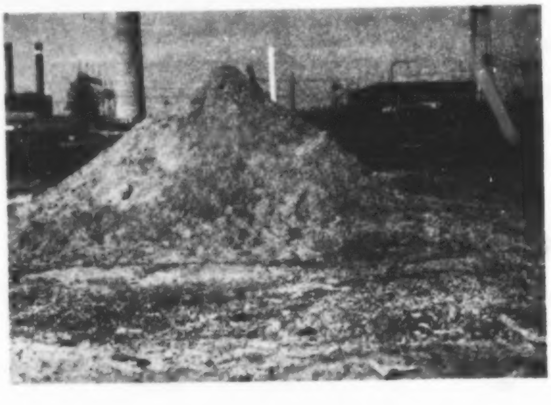


Figure 5. Pond H: gypsum filter cake immediately after placement

Figure 6. Pond B (Dravo): limestone, clarifier underflow, treated

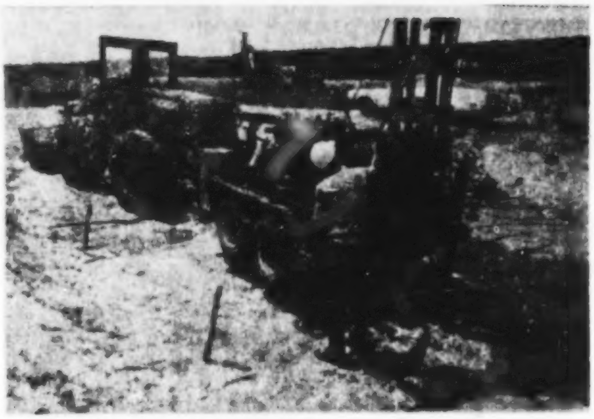


Figure 7. Pond C (IUCS): lime, centrifuge cake, treated

Figure 8. Pond E (Chemfix): limestone, clarifier underflow, treated

underflow was pumped directly into rotary mix trucks for transport to the pond. Fly ash, 40 weight percent (dry), was added to each truckload of sludge before it was discharged into the pond at 47-percent solids. The pond and its underdrain system are identical to that described for Pond G.

It was filled to a depth of 5 feet, which represents a total volume of approximately 147 cu yd. This pond will be used to evaluate the environmental acceptability of ash-free, limestone sludge remixed with fly ash and will also be tested for bearing-strength qualities as a landfill material.

### 2.3 GYPSUM (POND H)

Pond H was filled during the period of 18 August through 30 September 1977 with ash-free limestone sludge oxidized to sulfate. The fill was accomplished in two phases. In the first phase, the pond was filled to a depth of 4 feet with clarifier underflow, at 33-percent solids, to test its settling characteristics and load-bearing capacity with respect to time when underdrained, as well as the quality of the seepage water. This testing was performed over a two-week period. Immediately afterward, the second phase was begun. This consisted of constructing a 10-foot pile of the gypsum (99 percent) which had been filtered to an 86-percent solids content cake. The cake was dropped onto the near-center of the pond on a constant vertical line so that a natural cone was formed. The surface of the cone formed an angle of approximately 38 degrees with the horizontal. As placed, the dry cake is nonstructural. As it is rewetted, compression tests will be made on the site to determine the strength developed through natural compaction. The principal tests to be made on this cake will be (1) to determine the change in shape of the cone as it slumps and (2) to analyze runoff for suspended solids and water quality. Analyses of underdrainage water will continue.

The pond is the same size as Ponds F and G, and has a similar underdrainage system.

### 2.4 SCOPE OF THIS PAPER

The effort being reported upon in this paper is part of a broad range of FGD waste disposal study activities performed by Aerospace. The most recent work, described in Reference 3, provides the results of the chemical characterization and physical properties analyses for untreated and treated wastes from seven different scrubbers at eastern and western plants using lime, limestone, or double-alkali absorbents. It also provides cost estimates for the disposal of untreated waste in lined or unlined ponds and for the disposal of chemically treated waste. Therefore, the results described in this paper are oriented toward the specific activities at Shawnee; where appropriate, references have been made to relate this work to the general field of FGD waste disposal. Detailed results of the Shawnee disposal evaluation project are given in References 1 and 4.

## SECTION 3. INTERIM RESULTS

The results discussed in this paper generally encompass the data available through mid-1977. Physical and chemical characteristics of untreated and chemically treated sludges are discussed, as well as properties of sludges oxidized to gypsum, and untreated sludges disposed of in ponds fitted with an underdrainage system that collects leachate. In addition, a water balance and mathematical analysis of the underdrained system was conducted to illustrate its suitability as an environmentally acceptable disposal option. The chemical composition of the untreated sludges is summarized in Table 2. The project encompasses three lime sludges and five limestone sludges.

## 3.1 UNTREATED WASTES

Physical and chemical properties of untreated sludges were determined[3] and are presented in this paper. These include virtually all the properties needed to assess their disposal and land reclamation characteristics.

### 3.1.1 Physical Characteristics

The physical properties considered in the disposal of FGD sludges include bulk density, water retention characteristics, bearing strength, porosity, permeability, and viscosity. The latter is important in the transport of the sludge to a disposal site, and the others concern the weight and volume of the disposal material as well as the suitability of the waste as a load-bearing material and deterrent to seepage in a disposal site.

The physical properties of FGD sludges are dependent upon the characteristics of both the liquid and the solid constituents, as well as the interaction between them. The lime and limestone scrubber wastes contain four principal crystalline phases: calcium sulfite, calcium sulfate, fly ash, and unreacted limestone or precipitated calcium carbonate. In many cases, the sulfite phase also contains small fractions of sulfate crystals. However, the presence of the sulfate has not yet been found to affect the basic properties of the sludge.

3.1.1.1 Water Retention and Bulk Density. The water retention or, conversely, the dewatering characteristics of FGD wastes are important to the various disposal techniques in that they affect the volume of the disposal basin, the waste handling methods, and the condition of the wastes in their final disposal state. Bulk density is, then, a consequence of the dewatering characteristics of a sludge.

The effectiveness of the dewatering method used and the ability of a sludge to be dewatered is a function of a number of solids characteristics, including the size and distribution of particles, and the crystalline structure of the particles, which are a function of the system as well as its operating parameters. Data for four dewatering methods are reported: settling, settling by free drainage, vacuum filtration, and centrifugation; the results are based on laboratory experiments.

The highest density is obtained principally by vacuum-assisted filtration in most sludges and by centrifugation in a few cases. In all cases, relatively small density differences result from these two dewatering methods.

In most sludges, there is very little difference in the density when dewatered by settling or by settling combined with free drainage. While free draining may not produce a significant increase in bulk density, the slight gain coupled with the associated higher solids content may in some cases significantly increase load-bearing strength as discussed in Section 3.1.1.2.

Generally, the wet-bulk density ranged from a low of approximately 1.5 g/cm$^3$ (94 lb/ft$^3$) for settled sludges to a high of 1.65 g/cm$^3$ (103 lb/ft$^3$) for

## Table 2. CHEMICAL ANALYSIS OF UNTREATED SLUDGE SOLIDS

| Pond | Sludge Type | Solids Content, wt% | Calcium Sulfite, wt% | Calcium Sulfate, wt% | Calcium Carbonate, wt% | Fly Ash, wt % (dry) |
|---|---|---|---|---|---|---|
| A | Lime, filter cake | 46 | -- | -- | -- | - |
| B[a] | Limestone, clarifier underflow | 38 | 30.3 | 10.7 | 14.2 | 35 |
| C[a] | Lime, centrifuge cake | 55 | 38.8 | 9.7 | 0 | 40 |
| D | Limestone, clarifier underflow | 38 | 29.4 | 10.9 | 18.6 | 33 |
| E[a] | Limestone, clarifier underflow | 38 | 27.9 | 9.4 | 18.3 | 34 |
| F | Limestone, clarifier underflow, fly ash remixed | 47 | -- | -- | -- | 40 |
| G | Lime, centrifuge cake, fly ash layered | 47 | -- | -- | -- | 20 |
| H | Limestone[b], clarifier underflow | 33 | -- | -- | -- | ~0 |
| H | Limestone, filter cake | 86 | -- | -- | -- | ~0 |

[a] Subsequently, chemically treated.

[b] Subsequently, oxidized to gypsum.

-- To be analyzed

vacuum filtered (Table 3). Drained and centrifuged values were intermediate to these extremes, with drained being slightly higher than the settled, and centrifuged slightly lower than filtered. These values were obtained under laboratory conditions and may not necessarily be representative of results obtained from the use of commercial dewatering equipment.

3.1.1.2 Compressive and Load-Bearing Strength. The structural characteristics of wet FGD sludge affect its use where land reclamation is desired. Unconfined compressive strength of untreated wastes are low, and generally no specific values are reported because the material is usually too soft to measure. However, dewatering can produce improved structural qualities.

Load-bearing strength as a function of solids content of sludges dewatered by settling and draining are shown in Figure 9. These results reinforce previous observations of Mohave and Shawnee sludges,[5] indicating that they may be dewatered to critical and narrow ranges of solids content, above which the load-bearing strengths increase rapidly to values well above the minimum for safe access of personnel and equipment. However, the critical concentration appears to be unique for each type of sludge tested. In addition to providing data and load-bearing strengths of lime and limestone sludges (with and without fly ash), Figure 9 illustrates the effect of the absorbent and fly ash on dewatering characteristics. As contrasted to lime, limestone sludges are capable of being dewatered to higher solids contents, while the presence of fly ash enhances dewatering in both types of sludges. For any specific solids content of a given sludge, the load-bearing strength is less with fly ash than without.

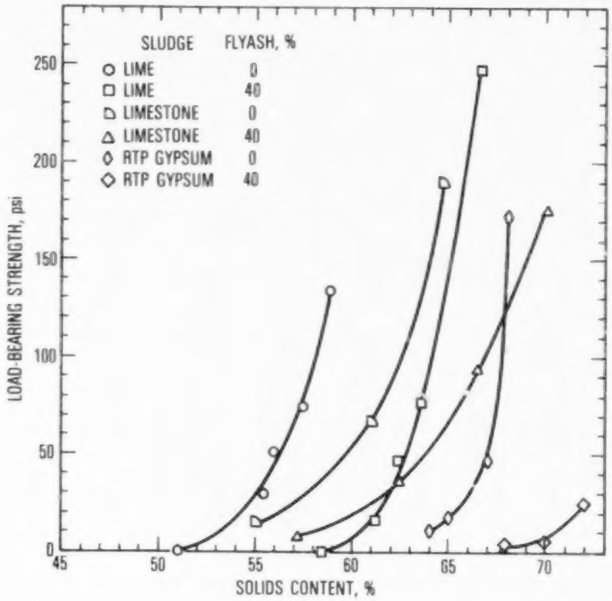


Figure 9. Load-bearing strength of Shawnee untreated wastes: laboratory data

Table 3. BULK DENSITIES OF FGD WASTES

| Sample Source and Date | Fly Ash, wt% (dry) | Dewatering Method[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Settled | | Settled and Drained | | Centrifuge | | Filter | |
| | | Solids, % | Density, g/cc | Solids, % | Density, g/cc | Solids, % | Density, g/cc | Solids, % | Density, g/cc |
| Shawnee Limestone, 2/1/73 | 20 | 49 | 1.45 | 56 | 1.51 | 60 | 1.56 | 65 | 1.65 |
| Shawnee Limestone, 6/15/74 | 40 | 53 | 1.46 | 58 | 1.53 | 63 | 1.60 | 66 | 1.64 |
| Shawnee Lime, 3/19/74 | 40 | 42 | 1.34 | 43 | 1.36 | 50 | 1.44 | 56 | 1.51 |
| Shawnee Lime, 9/8/76 | 40 | 45 | 1.34 | 58 | 1.50 | 53 | 1.44 | 61 | 1.54 |
| Shawnee Lime, 9/8/76 | ~ 0 | 47 | 1.37 | 51 | 1.41 | 48 | 1.38 | 57 | 1.49 |

[a] Using laboratory equipment.

The load-bearing strength of untreated sludges in undrained ponds, such as A and D, has been too low to support personnel (air-drying produced adequate strength in A, but it was lost upon rewetting). In preparation for the filling of Pond G, laboratory tests were conducted on ash-free lime sludge filter cake, remixed with fly ash in a quantity representing 40 weight percent of total solids; samples were allowed to settle or drain to obtain bearing-strength measurements as a function of draining time. The test results showed that undrained settling alone would not produce bearing strengths above 40 psi after a settling time of 13 days. Samples which were allowed to drain, however, showed significant increases in bearing strength within a short period of time. For example, samples in which half the fly ash was remixed in the sludge and the other half placed in layers showed bearing strengths greater than 20 psi in 12 hours and greater than 50 psi in 24 hours. The layering configuration was selected for the filling of Pond G, and it was demonstrated during filling that personnel could walk on the surface between 2 and 10 hours after placing the sludge and fly ash in the pond. Field evaluations of underdrained ponds of lime and limestone sludges have shown that these materials are capable of supporting light construction equipment within 12 hours after a heavy rain. High bearing strengths in excess of 50 psi were reached (Table 4). However, the need for layering sludge with fly ash may not be necessary; e.g., Pond F, which is not layered and has lower bearing-strength properties than Pond G, is nevertheless capable of supporting personnel and light construction equipment.

Laboratory analyses have indicated that limestone sludges produced at Shawnee typically have bearing strengths superior to that of Pond F. Therefore, further study will be conducted on bearing strength as a function of absorbent usage, scrubber operating parameters, resultant crystalline structure, and moisture content after drainage.

3.1.1.3 Permeability. The pollution potential of sludge liquor seeping into groundwaters is governed by the mobility of leaching waters; this mobility is limited by the coefficient of permeability of the various media through which this leachate must pass.

The permeation rate of leaching waters through the sludge defines an upper limit to the amount of leachate that enters the subsoil. The amount of liquid and the level of contamination of this liquid are jointly responsible for the pollution potential of any given waste disposal site.

The permeability coefficient of untreated wastes containing fly ash are approximately $2 \times 10^{-4}$ cm/sec (Table 5). The permeability coefficient of untreated sludges has been shown to be a function of the volume fraction of solids in the waste. These values are intermediate to typical values for silty sand and sandy clay, which are $10^{-4}$ cm/sec and $5 \times 10^{-6}$ cm/sec, respectively.[6]

Consolidation of untreated wastes under pressures of 30 to 100 psi reduced the void fraction and also reduced permeability coefficients by a factor of from 2 to 5 (Table 6). The higher solid volume fraction, resulting from compaction or consolidation, and the resultant decrease in permeability appear to be functions of the size of the sludge particles and the size and distribution of the fly ash particles. Consolidation of untreated sludge at the base of a 40-foot deep disposal site may decrease permeabilities to about $10^{-5}$ cm/sec as compared with $10^{-4}$ cm/sec at the surface.

## Table 4. SLUDGE BEARING STRENGTH

| Pond and Absorbent | Bearing Strength, psi[a] | | |
|---|---|---|---|
| | Distance Below Sludge Surface | | |
| | 1-2 in. | 2-4 in. | 4-6 in. |
| Pond B[b] (Dravo), Lime | 10-15 | 150 | 150-300 |
| Pond C (IUCS), Limestone | 150-330 | 240-300 | 330 |
| Pond E (Chemfix), Limestone | 75-300 | 90-300 | 300-330 |
| Pond F,[c] Limestone | 50-75 | 60-75 | 60-75 |
| Pond G,[c] Lime | 100-150 | 100-150 | 180-240 |
| Pond H,[c] Gypsum[d] | 330 | 330 | >330 |
| Soil (Shawnee, Clay) | 60-100 | 120 | 240-300 |

[a] Data taken in August 1977 within 24 hr following a 3.3-in. rainfall.

[b] Pond B covered by 4 in. of water.

[c] Untreated, underdrained.

[d] Tests for Pond H made on settled and drained clarifier underflow.

Table 5. PERMEABILITY OF SHAWNEE SLUDGES[a]

| Sludge[b] | Void Fraction | Permeability Coefficient, cm/sec |
|---|---|---|
| Lime | 0.75 | $1.8 \times 10^{-4}$ |
| Limestone | 0.69 | $2.0 \times 10^{-4}$ |

[a] Reference 3.

[b] All samples contain fly ash (40 wt%) (dry).

Table 6. EFFECT OF COMPACTION ON PERMEABILITY OF UNTREATED SLUDGE

| Sludge | Void Fraction | Permeability Coefficient, cm/sec |
|---|---|---|
| Lime | 0.75 | $1.8 \times 10^{-4}$ |
| | 0.68 | $6.0 \times 10^{-5}$ |
| | 0.60 | $1.4 \times 10^{-5}$ |
| | 0.54 | $7.3 \times 10^{-6}$ |
| Limestone | 0.69 | $2.0 \times 10^{-4}$ |
| | 0.56 | $6.0 \times 10^{-5}$ |

Chemical treatment tends to reduce permeability by less than a factor of two in some cases and by several orders of magnitude in others (Section 3.2).

3.1.1.4 Viscosity. The viscosity of the sludge is indicative of its pumpability, which affects both the mode and cost of sludge transport. The results of viscosity tests for various sludges from the Shawnee test facility show that easily pumpable mixtures (less than 20 poise) range from a high solids content of 55 weight percent to a low solids content of 40 weight percent (Figure 10).

The wastes produced in FGD systems contain finely divided particulate matter suspended in an aqueous medium and consist of three major phases having markedly different morphologies: calcium sulfite hemihydrate, calcium sulfate dihydrate, and fly ash. It is both the particle size distribution and phase morphology that are believed to influence the viscosity of the sludges.

Both calcium sulfate and sulfite scrubber waste products tend to have particle sizes in the same range as fly ash, between 1 and 100 μm. However, fly ash is formed as spheres, while sulfite wastes are platelets (limestone) or rosettes (lime), and sulfates are blocky in shape. Unreacted $CaCO_3$ from the limestone (or precipitated from the lime process) is usually present in the waste and contributes an additional shape parameter. The data clearly suggest that fly ash decreases the viscosity of a sludge, e.g., the effect of limestone sludge containing 40, 20, and <1 percent fly ash and lime with 40 and <1 percent fly ash (Figure 10). It was also observed that the presence of fly ash has a more marked effect in reducing the viscosity of limestone sludges than in the lime sludge.

| CURVE | SOURCE | DATE | FLY ASH, % |
|---|---|---|---|
| 1 | TVA SHAWNEE LIMESTONE | 7/11/73 | 40.9 |
| 2 | TVA SHAWNEE LIMESTONE | 6/15/74 | 40.1 |
| 3 | TVA SHAWNEE LIMESTONE | 2/1/73 | 20.1 |
| 4 | TVA SHAWNEE LIME | 9/8/76 | 40.0 |
| 5 | TVA SHAWNEE LIME | 3/19/74 | 40.5 |
| 6 | TVA SHAWNEE LIMESTONE | 9/28/76 | <1 |
| 7 | TVA SHAWNEE LIME | 9/8/76 | <1 |

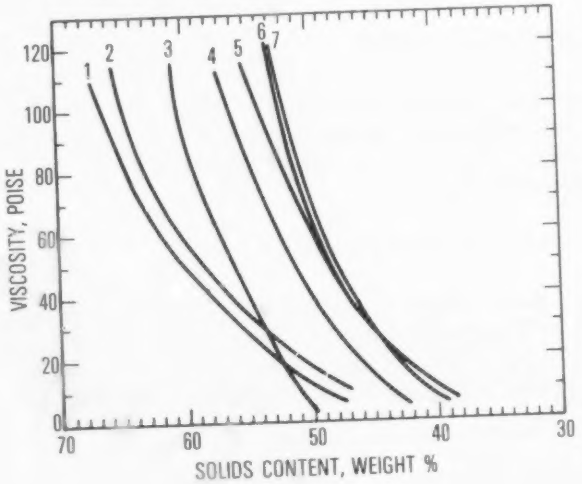


Figure 10. Viscosity of Shawnee FGD sludges

### 3.1.2 Chemical Characteristics of Untreated Sludges

3.1.2.1 Major Chemical Constituents. The composition of the solids fraction of sludges sampled was determined by chemical means and is presented in Table 2.

In the sludge solids, gypsum and calcium sulfite hemihydrate are the principal sulfur-containing products, as well as a broad range of fly ash resulting from either separate or simultaneous fly ash collection. The presence of limestone in all samples is a consequence of both unreacted limestone absorbent and calcium carbonate formed by lime absorbing carbon dioxide from the atmosphere.

3.1.2.2 Pond Input Liquor Composition. The composition of the sludge input liquor is shown in Table 7.[7] Leachate concentrations of the various constituents are generally compared to these values.

3.1.2.3 Leachate. The analyses of leachate from Ponds A/A1 and D show that the concentrations of total dissolved solids (TDS) increased steadily after filling, and after a period of approximately 40 weeks (during which the leachate was diluted with rainwater initially present in the well area) reached peak levels very close to those measured in the input liquor (Figures 11 and 12). Thereafter, the TDS and chloride levels dropped steadily in both ponds. The concentrations of six minor constituents of interest, arsenic, boron, lead, magnesium, mercury, and selenium, are shown in Table 8; these were relatively constant over most of the period monitored. For comparative purposes the concentrations of minor species in chemically treated sludge leachate are also shown.

3.1.2.4 Supernate. The TDS and the concentrations of major constituents in the supernates of these ponds decreased with time from initial values corresponding to the values measured in the input liquor. After the initial decrease, fluctuations were observed in which concentrations increased during dry weather as a result of net water loss by evaporation and decreased again when increased rainfall caused additional dilution.

3.1.2.5 Groundwater. The analysis of groundwater shows no indication of increases in concentration levels attributable to the ponds.

## 3.2 TREATED SLUDGE

Laboratory tests were performed on core samples removed from ponds containing treated sludge to determine the physical and leaching characteristics of these materials. Results of measurements taken through July 1977 are given in the paragraphs that follow.

### 3.2.1 Physical Characteristics

The results show no apparent time-dependent trends in the permeability of these sludges. Typical permeability coefficients ranged from $7 \times 10^{-5}$ cm/sec for Pond B, to $2 \times 10^{-5}$ cm/sec for Pond E, and $5 \times 10^{-5}$ cm/sec for Pond C, with selected crack-free samples exhibiting coefficients of 3 to $5 \times 10^{-7}$ cm/sec (Table 9).

Typical moisture content for the cores from the three ponds were 54 percent for B, 39 percent for C, and 49 percent for E. Average void fractions

## Table 7. INPUT LIQUOR ANALYSIS

| Pond[a] | Sludge Type | Moisture Content, % | pH | Concentration, mg/ℓ | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ca | $SO_4$ | Cl | $SO_3$ | TDS[b] | As | B | Pb | Mg | Na | Se | Hg | COD[c] |
| A | Lime, filter cake | 54 | 8.3 | 2100 | 1525 | 4600 | 4 | 8560 | 0.024 | 44 | 0.49 | 290 | -- | 0.005 | <0.0001 | -- |
| B | Limestone, clarifier underflow | 62 | 8.9 | 1060 | 1875 | 1850 | 3 | 5160 | 0.004 | 97 | <0.02 | 2.5 | 17 | 0.020 | 0.0024 | 140 |
| C | Lime, centrifuge cake | 45 | 8.9 | 2720 | 1575 | 4700 | 45 | 9240 | 0.002 | 34 | <0.01 | 33 | 46 | 0.018 | <0.0001 | 140 |
| D | Limestone, clarifier underflow | 62 | 9.2 | 1880 | 1500 | 2950 | 56 | 6750 | -- | 93 | <0.02 | 50 | 56 | -- | -- | 130 |
| E | Limestone, clarifier underflow | 62 | 9.4 | 1880 | 1400 | 2700 | 32 | 6190 | 0.004 | 80 | <0.01 | 12 | 41 | 0.014 | 0.00033 | 110 |
| F | Limestone, clarifier underflow, flyash remixed | 53 | 12.2 | 1990 | 1100 | 2000 | -- | 6700 | 0.002 | 76 | <0.01 | 0.3 | 70 | 0.042 | <0.0002 | 43 |
| G | Lime, centrifuge cake, flyash remixed and layered | 53 | 7.8 | 150 | 6600 | 3600 | -- | 14000 | 0.14 | 93 | <0.01 | 5000[d] | 12 | 0.63 | <0.0002 | 53 |

[a] Pond H to be analyzed.

[b] Total dissolved solids.

[c] Chemical oxygen demand.

[d] Magnesia added to lime absorbent.

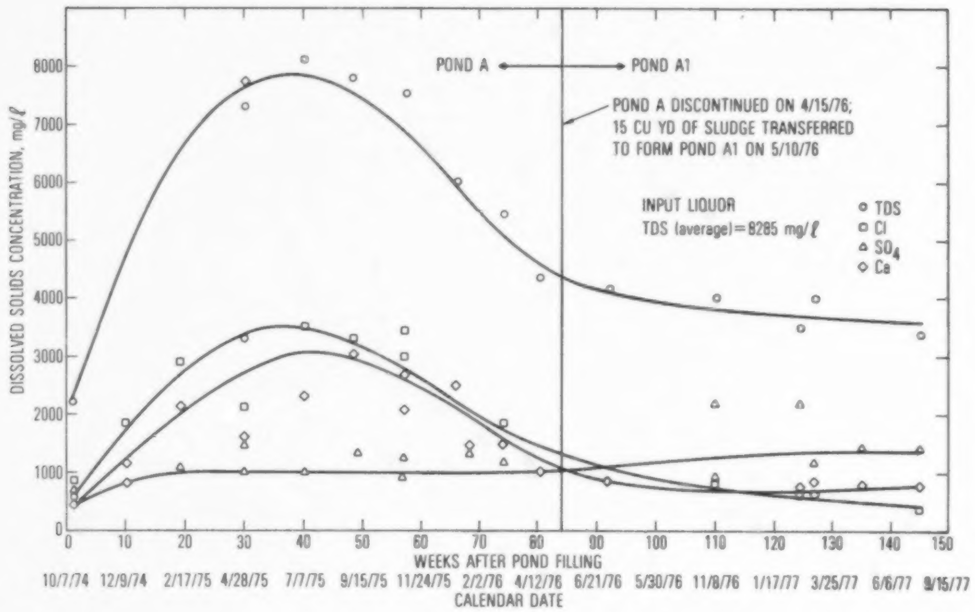


Figure 11. Concentration of TDS and major species in Pond A leachate

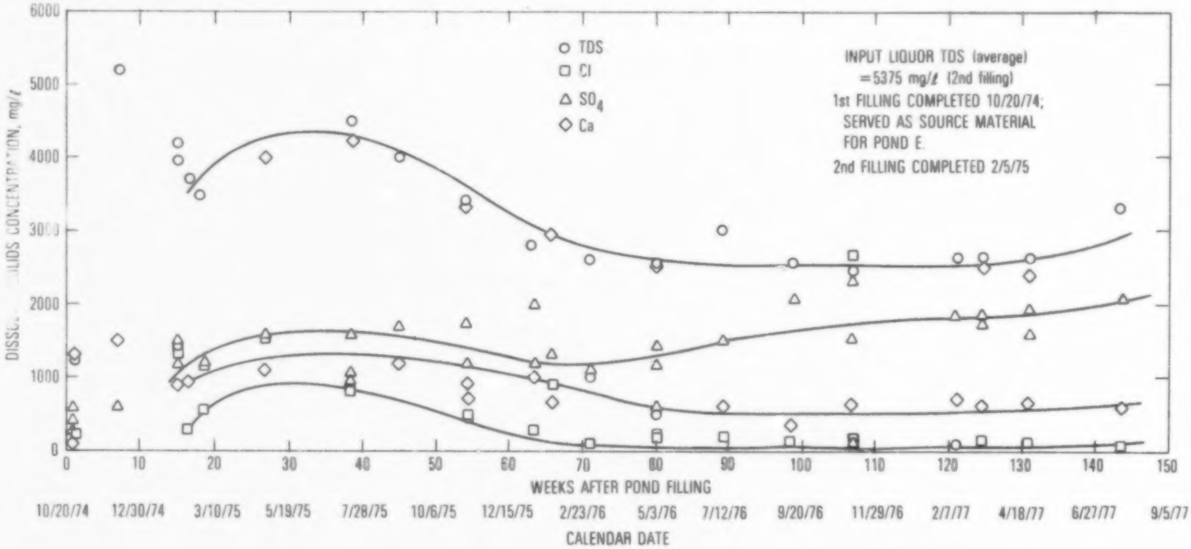


Figure 12. Concentration of TDS and major species in Pond D

## Table 8. CONCENTRATION OF MINOR CONSTITUENTS IN LEACHATE

| Element | Concentration, mg/ℓ[a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Untreated Sludge | | | | Chemically Treated Sludge | | | | | |
| | Ponds A and A1 | | Pond D | | Pond B | | Pond C | | Pond E | |
| | Input Liquor | Leachate | Input Liquor | Leachate | Input Liquor | Leachate | Input Liquor | Leachate | Input Liquor | Leachate |
| Arsenic | 0.024 | 0.008 | 0.004 | 0.3 | 0.004 | 0.03 | 0.002 | 0.02 | 0.003 | 0.005 |
| Boron | 44 | 30 | 93 | 20 | 97 | 1.5 | 34 | 2 | 80 | 0.05 |
| Lead | 0.49 | 0.05 | <0.02 | 0.04 | <0.02 | 0.04 | <0.01 | 0.02 | <0.01 | 0.04 |
| Magnesium | 290 | 60 | 50 | 50 | 2.5 | 30 | 33 | 10 | 12 | 2 |
| Mercury | <0.0001 | 0.001 | 0.00033 | 0.0007 | 0.00024 | 0.0006 | <0.00008 | 0.0005 | 0.00033 | 0.001 |
| Selenium | 0.005 | 0.005 | 0.014 | 0.01 | 0.02 | 0.015 | 0.018 | 0.015 | 0.014 | 0.01 |

[a] The concentrations shown above were taken from the approximate midpoint of the range of concentrations observed since the ponds were put in operation.

Table 9. PHYSICAL CHARACTERISTICS OF IMPOUNDED TREATED SLUDGE CORES

| Pond | Coring Date | Moisture Content, wt % | Density, g/cm$^3$ (wet) | Unconfined Compressive Strength, lb/in$^2$ (wet) | Density, g/cm$^3$ (dry) | Porosity, void fraction (volumetric) | Permeability Coefficient, cm/sec |
|---|---|---|---|---|---|---|---|
| B | 5/29/75 | 49 | 1.43 | 62 | 0.73 | 0.71 | -- |
| B | 6/12/75 | 58 | 1.40 | 30 | 0.61 | 0.76 | $6.9 \times 10^{-5}$ |
| B | 7/30/75 | 56 | 1.30 | 28 | 0.56 | 0.77 | $1.4 \times 10^{-4}$ |
| B | 1/14/76 | 54 | 1.37 | 84 | 0.63 | 0.75 | $3.8 \times 10^{-5}$ |
| C | 5/29/75 | 37 | 1.69 | 462 | 1.07 | 0.58 | $5.5 \times 10^{-5}$ |
| C | 6/12/75 | 41 | 1.42 | 321 | 0.80 | 0.68 | $5.5 \times 10^{-7}$ |
| C | 1/14/76 | 39 | 1.50 | 40 | 0.91 | 0.64 | $3.2 \times 10^{-7}$ |
| C | 7/7/76 | 38 | -- | -- | -- | -- | $5.4 \times 10^{-5}$ |
| C | 3/15/77 | 38 | 1.50 | -- | -- | -- | $5.6 \times 10^{-5}$ |
| E | 2/27/75 | 51 | 1.43 | 118 | 0.71 | 0.72 | $1.5 \times 10^{-5}$ |
| E | 2/27/75 | -- | -- | -- | -- | -- | $2.7 \times 10^{-5}$ |
| E | 7/29/75 | -- | -- | -- | -- | -- | $9.3 \times 10^{-5}$ |
| E | 1/14/76 | 48 | 1.43 | 24 | 0.74 | 0.70 | $1.2 \times 10^{-5}$ |
| E | 7/7/76 | 51 | -- | -- | -- | -- | $5.7 \times 10^{-6}$ |
| E | 3/15/77 | 47 | 1.30 | -- | -- | -- | $1.6 \times 10^{-6}$ |

were 0.75, 0.66, and 0.70 for Ponds B, C, and E, respectively. The advantages of reduced permeability and proper site management to reduce or eliminate seepage are discussed in Section 4.1.

Bulk densities in the as-received wet condition were approximately twice the corresponding dry densities for Ponds B and E, e.g., 1.4 versus 0.7 g/cm$^3$. For Pond C, with slightly higher bulk densities, the average value for the as-received condition was approximately one and one half times as great as that of the dry material, e.g., 1.5 versus 0.9 g/cm$^3$.

The compressive strengths of free-standing as-received samples of these same materials ranged from 40 to 462 psi for Pond C, 28 to 84 psi and 24 to 118 psi for Ponds B and E, respectively (Table 9). In situ bearing-strength tests showed high values for all chemically treated ponds (Table 4).

### 3.2.2 Leaching Characteristics

3.2.2.1 Laboratory Results. Leaching tests were conducted in the laboratory on cores taken from ponds containing chemically treated sludges, on samples that were sufficiently intact. Deionized water was passed through the core segments under applied pressure of 5 psi, and incremental volumes of leachate were collected and analyzed for major liquor constituents and for TDS.

Leaching data have been plotted in Figure 13 for a Pond B core. Leaching was continued until more than 8 pore volumes had been eluted. The chloride concentration in the final leachate sample was less than 1/10 of that in the input liquor; the calcium and sulfate concentrations were only moderately lower. Solubility calculations demonstrate that both leachate samples were effectively saturated with gypsum, $CaSO_4 \cdot 2H_2O$.

For the Pond C core of May 1975 (Figure 14), leaching was continued until 27 pore volumes had been eluted. The TDS and chloride concentrations in the final eluted volume had decreased about 15-fold from the initial values, which were approximately half the concentrations in the pond input liquor prior to treatment. The decreases in concentrations of sulfate and calcium were only 3- to 5-fold.

The leaching tests of Pond E cores were carried out until 9 to 10 pore volumes had been eluted. The final samples eluted showed concentrations that were approximately 10-fold lower than the initial concentrations, which were approximately half those of the pond input liquor, except for calcium (Figure 15). Calcium concentrations were very low in leachates from the Pond E chemically treated sludge, presumably because of ion exchange with sodium, which is predominant in this treatment process.

3.2.2.2 Field Results. The analyses of leachate well samples from the ponds containing treated sludge show data trends similar to the untreated ponds (Section 3.1.2.3); however, the concentrations of the major constituents and TDS consistently remain at levels approximately one half that of those found in the input liquor (Table 7). The results of these analyses are presented in Figures 16 through 18 for Ponds B, C, and E, respectively.

Six selected minor constituents of interest, i.e., arsenic, boron, lead, magnesium, mercury, and selenium, remained at relatively constant levels throughout the monitoring period, with the exception of the boron level in Pond C, which increased steadily to a level approaching that of the input liquor. The reason for this increase has not been determined.

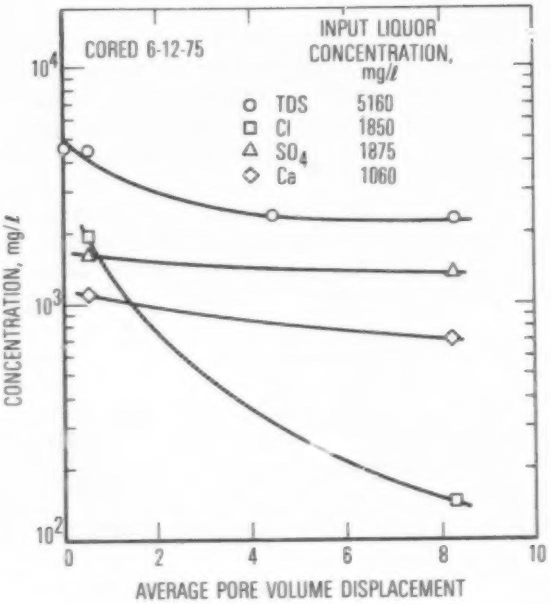


Figure 13. Concentration of TDS and major species in Pond B sludge core leachate

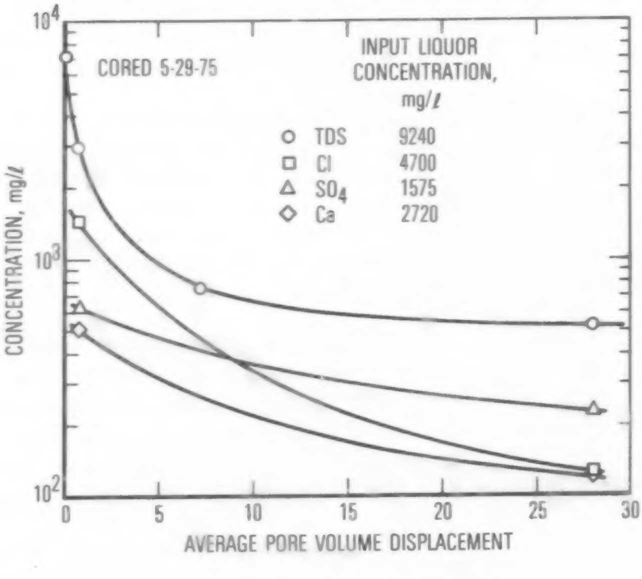


Figure 14. Concentration of TDS and major species in Pond C core leachate

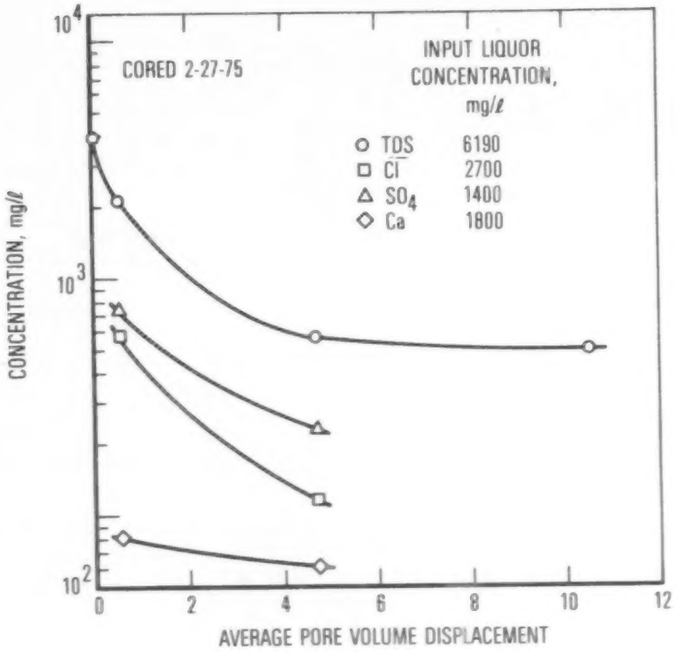


Figure 15. Concentration of TDS and major species in Pond E sludge core leachate

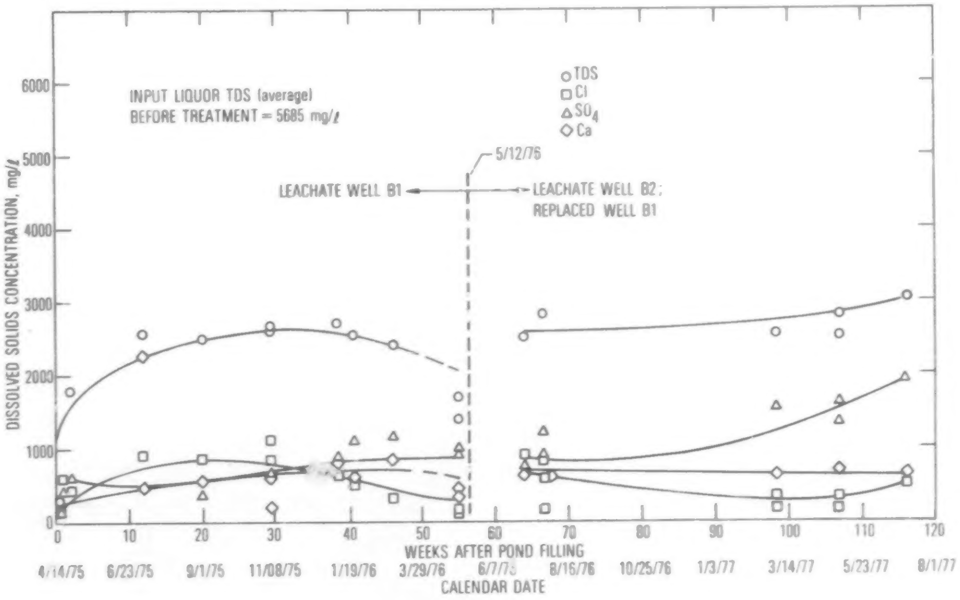


Figure 16. Pond B leachate TDS

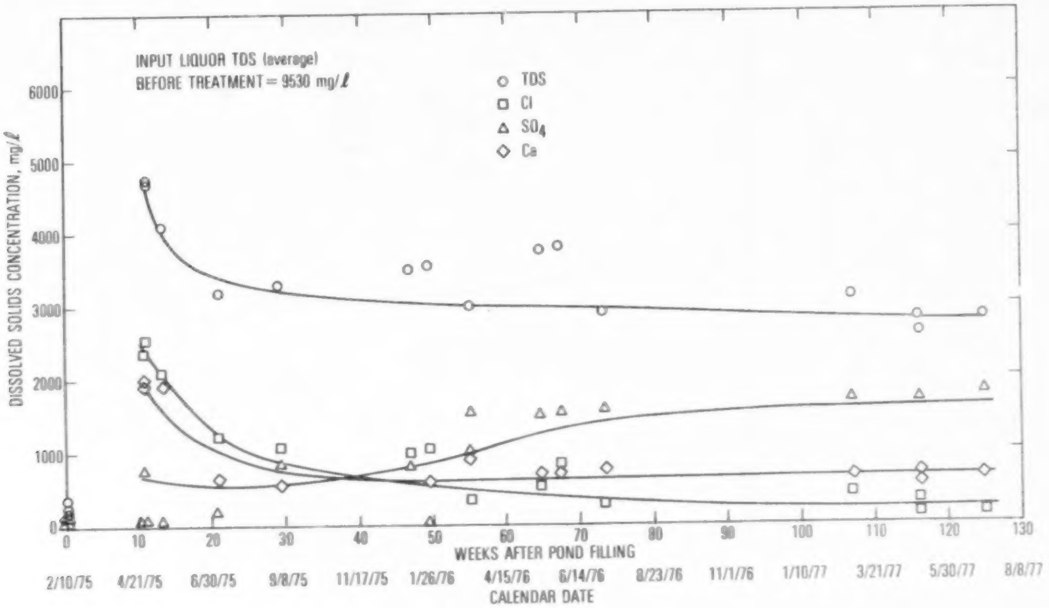


Figure 17. Pond C leachate TDS

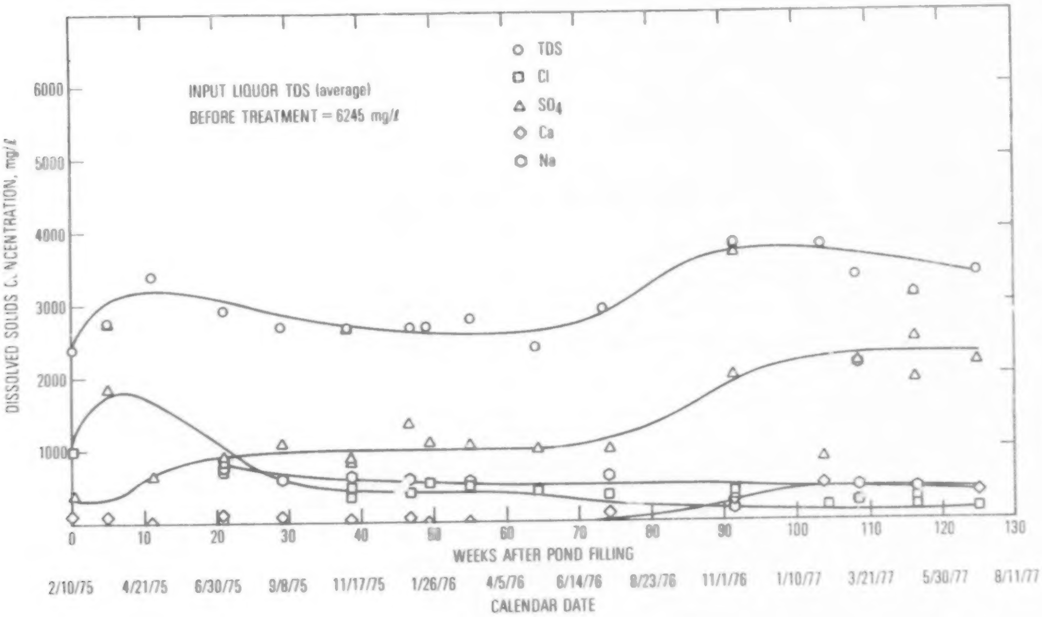


Figure 18. Pond E leachate TDS

## 3.3 GYPSUM FROM FORCED OXIDATION OF LIMESTONE SCRUBBER SLUDGE

R. Borgwardt of EPA, RTP, has been conducting pilot-plant-scale experiments, evaluating the forced oxidation of sulfite sludges from the limestone and lime scrubbing of $SO_2$ from flue gas.[8] The experiments were designed to determine limestone utilization, oxidation efficiency, settling rates, and bulk densities of the gypsum, and they provided data for use in operating a scrubber system at Shawnee. Gas-burner combustion products were used to simulate flue gas, and $SO_2$ and HCl were introduced into the gas stream of the pilot plant system, which consisted of a first-stage spray tower and a second-stage TCA loop. Fly ash and limestone were introduced in the second-stage loop. The first-stage loop contained a provision for air sparging to oxidize the calcium sulfite. A portion of the oxidized slurry was bled off to a vacuum drum filter.

To augment the numerous chemical analyses and physical property measurements being made at RTP and reported by Borgwardt, Aerospace conducted additional characterization tests on the gypsum filter cake and slurries from the first-stage loop. Samples were analyzed from tests that used limestone scrubbing, one with and the other without added fly ash. Wet chemical analyses were made for major constituents of the solid and liquid phases and leachates (Tables 10 and 11). Physical properties such as bulk densities, compressive strengths, and permeabilities were also measured (Table 12).

Field data are not reported because gypsum from the Shawnee evaluation tests was placed in Pond H in September 1977, and results were unavailable during the preparation of this paper.

### 3.3.1 Chemical and Leaching Characteristics

The chemical analysis of the solids is presented in Table 10. It was shown that (1) both the first-stage slurry and the filtered solids were primarily gypsum with small amounts of $CaSO_3 \cdot 1/2H_2O$ and (2) the filtered solids contained more $CaSO_3 \cdot 1/2H_2O$ than the first-stage slurry. Although the filter cake contained primarily gypsum, approximately 5-percent calcium sulfite was observed in each of the two samples analyzed. The presence of sulfite in the filter cake was not the result of incomplete oxidation in the first-stage loop nor indicative of the basic characteristics of the process, but was determined to be the result of an unscheduled modification of the plumbing whereby a portion of the second-stage slurry was used to bypass the first-stage loop as a means to control the solids content in the second stage. In addition, the quantitative results of the wet chemical analyses verified conclusively that complete oxidation of calcium sulfite to gypsum was achieved in the first-stage loop.

3.3.1.1 Leaching Test Results. The Aerospace leaching test results of the major species from the RTP limestone-scrubbed FGD gypsum from sludge samples with fly ash and without fly ash are outlined in Table 11.

In assessing the overall material balance at pore volume displacements (PVDs) of less than 1.0, i.e., TDS versus calcium, sulfate, chlorine, and magnesium, better agreement was obtained with those samples without fly ash than those that had fly ash in the scrubber slurry. This indicates that the major species were primarily calcium, sulfate, chlorine, and magnesium for the no-fly-ash case, whereas some significant additional constituents were probably leached when fly ash was present. It is also apparent that, after many PVDs

Table 10. COMPOSITION OF RTP OXIDIZED LIMESTONE SOLIDS BY WET CHEMICAL ANALYSIS

| Sample Designation | Total Solids, % | | Composition of Solids, wt % (dry) | | | |
|---|---|---|---|---|---|---|
| | Slurry | Filter Cake[a] | Fly Ash | Gypsum | Calcium Sulfite | Calcium Carbonate |
| Sampled 9/30/75, Contained Fly Ash | | | | | | |
| First-Stage Gypsum Slurry | 11.3[b] | 90 | 40.0 | 62.5 | <0.5 | <0.5 |
| RTP Gypsum Filter Cake | 64.9 | 82 | 38.6 | 52.7 | 5.7 | 4.9 |
| Sampled 12/4/75, Contained No Fly Ash | | | | | | |
| First-Stage Gypsum Slurry | -- | 85 | -- | 94.6 | 0.7 | 6.0 |
| RTP Gypsum Filter Cake | -- | 82 | -- | 86.4 | 4.5 | -- |

[a] Laboratory filtration.

[b] As-received at Aerospace.

-- Not determined.

# Table 11. ANALYSIS OF LEACHATES OF GYPSUM SAMPLES FROM RTP FORCED OXIDATION TESTS

| Sample | Fly Ash, wt % (dry) | Pore Volume Displacements | Concentration, mg/ℓ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | TDS | TDS Corrected[a] | $\Sigma$[b] | $Ca^{++}$ | $SO_4^=$ | $Cl^-$ | $Mg^{++}$ |
| First Stage Gypsum Slurry | 40 | 0.7<br>18.0 | 6820<br>2180 | 5840<br>2140 | 5140<br>2130 | 1300<br>550 | 1540<br>1500 | 2000<br>80 | 300<br>0.3 |
| First Stage Gypsum Slurry | 0 | 1.0<br>10.3 | 5860<br>2160 | 4775<br>2120 | 5110<br>1620 | 1280<br>540 | 1450<br>1000 | 2160<br>80 | 220<br>0.04 |
| RTP Gypsum Filter Cake | 39 | 0.6<br>11.0 | 7100<br>2190 | 6010<br>2130 | 5470<br>2065 | 1220<br>560 | 1600<br>1400 | 2220<br>90 | 430<br>15 |
| RTP Gypsum Filter Cake | 0 | 0.5<br>14.0 | 10,100<br>2310 | 8100<br>2260 | 7940<br>2100 | 2170<br>500 | 1250<br>1500 | 4040<br>100 | 480<br>0 |

[a] Corrected for $2H_2O$ in $CaCl_2 \cdot 2H_2O$.

[b] Sum of $Ca^{++}$, $SO_4^=$, $Cl^-$, $Mg^{++}$.

Table 12. PHYSICAL CHARACTERISTICS OF RTP OXIDIZED LIMESTONE SLUDGE SOLIDS

| Sample | Moisture Content, % | Density, g/cm$^3$ (wet) | Unconfined Compressive Strength, psi (wet) | Porosity (Void Fraction) | Permeability Coefficient, cm/sec |
|---|---|---|---|---|---|
| Sampled 9/30/75, Contained Fly Ash | | | | | |
| Filtered First-Stage Gypsum Slurry[a] | 10 | 1.4 | 62 | 0.50 | $1.6 \times 10^{-4}$ |
| RTP Gypsum Filter Cake[b] | 18 | 1.5 | 20 | 0.50 | $4.5 \times 10^{-5}$[c] |
| Sampled 12/4/75, Contained No Fly Ash | | | | | |
| Filtered First-Stage Gypsum Slurry[a] | 15 | 1.3 | 60 | 0.55 | $1.1 \times 10^{-4}$ |
| RTP Gypsum Filter Cake[b] | 18 | 1.35 | 25 | 0.55 | $1.1 \times 10^{-4}$ |

[a] See Table 10.

[b] Contaminated gypsum with 5% calcium sulfite (Table 10).

[c] Test specimen was prepared by "rodding" slurry during initial drainage.

(>10), the concentrations of the major species were virtually the same whether or not fly ash was initially present.

On the basis of the drying conditions used in the TDS determination, it was found that the $CaCl_2 \cdot 2H_2O$ in the solids was not dehydrated when the sample was brought to constant weight. A correction to reduce the TDS by the amount of $H_2O$ in the hydrated $CaCl_2$ was applied and is shown in Table 11.

The results for the RTP gypsum filter cake and solids from the first-stage gypsum slurry show that after 2 to 3 PVDs of water have passed through the samples, gypsum, which is the principal constituent in both materials, is being dissolved to produce a leachate that is saturated with calcium and sulfate ions. Also, comparing results from Table 11 (gypsum) and Table 7 (high sulfite), it is seen that the major constituents in leachates from these different types of material are similar.

### 3.3.2 Physical Characteristics

Measurements were made of permeability coefficients, void fraction, water retention, density, unconfined compressive strength, and load-bearing strength of filtered first-stage gypsum slurry and RTP gypsum filter cake containing about 5-percent calcium sulfite, both with and without fly ash. A summary of the physical properties is provided in Table 12. Significant results are as follows: Permeability coefficients for the gypsum and gypsum with calcium sulfite were approximately $10^{-4}$ cm/sec. The presence of fly ash made no appreciable difference.

The void fractions of these solids were approximately 0.5, and densities ranged from 1.3 to 1.5 g/cm$^3$. Fly ash appears to decrease porosity by approximately 10 percent and to increase density by about 10 percent.

A comparison of the results of unconfined compressive strength measurement for the two sets of samples (with and without fly ash) shows that the corresponding solids in both sets have comparable strength. Furthermore, for both sets of samples, the first-stage solids (gypsum) showed substantially higher unconfined compressive strength than the RTP gypsum filter cake, which contained about 5-percent sulfite.

It should be noted that the unconfined compressive strength of the RTP gypsum filter cake which contained about 5-percent calcium sulfite was approximately equal to that of a sludge that is predominantly calcium sulfite.[9] The presence of fly ash did not seem to affect the unconfined compressive strength of the materials; however, it had a negative effect on bearing strength, as noted below.

Load-bearing strength measurements, using a modified California bearing ratio test, were made on the filter cake samples (gypsum with about 5-percent calcium sulfite), with and without fly ash. Values of 20 psi were observed for both samples when the moisture content was 71.5 and 65 percent, respectively (Figure 9). Dewatering of the fly-ash-free sample was continued, and approximately 185 psi was observed at 68-percent solids. Although data were not obtained at higher solids content for the sample containing fly ash, the similarity of the curves indicates that the onset of high strength for the fly ash material is in the range of 72- to 73-percent solids.

## SECTION 4. PRELIMINARY ASSESSMENT

### 4.1 ENVIRONMENTAL BENEFITS OF CHEMICAL TREATMENT

Chemical treatment has been found to have major benefits which effectively minimize (and possibly, in some cases, virtually eliminate) the release of leached sludge constituents to the subsoil through (1) the decreased permeability of the treated material, and (2) the amenability of the treated material to compaction and contouring during placement so that standing water does not occur on the disposal site. The prevention of standing water avoids having a hydraulic head on the site and, therefore, seepage through the pores does not occur as a result of hydraulic pressure. This is accomplished by managing the site so that a major portion of the rainfall on such a site runs off and is collected in a peripheral ditch which directs the water to a settling pond, from which decanted liquor is disposed of in an adjacent stream, if acceptable, or returned to the power plant water reuse system (see Reference 2 for a discussion of site management).

Various examples illustrating the effects of sludge treatment, the effects of different subsoils, and management of the site for different rainfall recharge rates are presented. The relative amounts of sludge constituents (TDS) released at the sludge base, for different modes of disposal were calculated (Table 13 and Figure 19). This analysis is based on correlations of laboratory results and Shawnee field condition data reported in this paper and, also, in Reference 3. All the cases are indexed to an untreated slurry pond, namely, Case 1, in which the soil permeability coefficient is $10^{-5}$ cm/sec.

In assessing the effectiveness of chemical treatment, tests to determine permeability of chemically treated sludges were performed on cores extracted from the Shawnee field evaluation site. Constant head permeability tests were run on (1) pulverized samples, and (2) samples with and without visible cracks. Uncracked samples of one material had coefficients of permeability of about $10^{-7}$ cm/sec; and the pulverized and the cracked samples had coefficients of approximately $10^{-5}$ cm/sec. Therefore, the effective coefficient of the treated material could be expected to be between $10^{-5}$ and $10^{-7}$ cm/sec. Assuming a conservative case (using a coefficient of $10^{-5}$), an order of magnitude improvement in impermeability is realized compared to untreated sludges, which typically have a coefficient of about $10^{-4}$.

The systematic reduction of standing water is illustrated in Cases 3 through 5, wherein the recharge rate is reduced compared to a ponded slurry. If only unevaporated rainfall is allowed to recharge, the mass release into the subsoil is reduced by a factor of about 5 (Case 3 versus 1, and Case 4 versus 2).

The significance of eliminating standing water by runoff is also shown. If it is assumed that 10 percent of the net rainfall is recharged, then a one order of magnitude reduction is achieved relative to a dewatered and ponded treated waste (Case 5 versus 4), and two to three orders of improvement depending on soil permeability when comparing the mass seepage from a chemically treated site to that of a ponded untreated site (Case 5 versus 1). In addition, compacting the treated materials during the site filling may reduce crack formation so that an effective coefficient of permeability better than $10^{-5}$ cm/sec may be realized.

Table 13. CASE STUDIES FOR COMPARISON OF MASS RELEASE OF SLUDGE CONSTITUENTS FOR VARIOUS DISPOSAL ALTERNATIVES

| Case | Disposal Method[a] | Surface Water | Sludge Condition[b] | Sludge Permeability, cm/sec |
|---|---|---|---|---|
| 1 | Ponded slurry | Constant supernate[c] | Untreated | $10^{-4}$ |
| 2 | Ponded slurry | Constant supernate | Chemically treated | $10^{-5}$ |
| 3 | Ponded cake | 10-in/yr recharge[d] | Untreated | $10^{-4}$ |
| 4 | Dewatered and ponded | 10-in/yr recharge[d] | Chemically treated | $10^{-5}$ |
| 5 | Landfill | 1-in/yr recharge[e] | Chemically treated | $10^{-5}$ |

[a] Fill period = 5 yr; depth = 30 ft.

[b] Porosity (void volumetric fraction) = 0.67.

[c] Constant supernate assumes 1-ft depth of surface water.

[d] 10-in/yr recharge is unevaporated rainfall.

[e] 1-in/yr effective recharge resulting from seepage during runoff of rainfall.

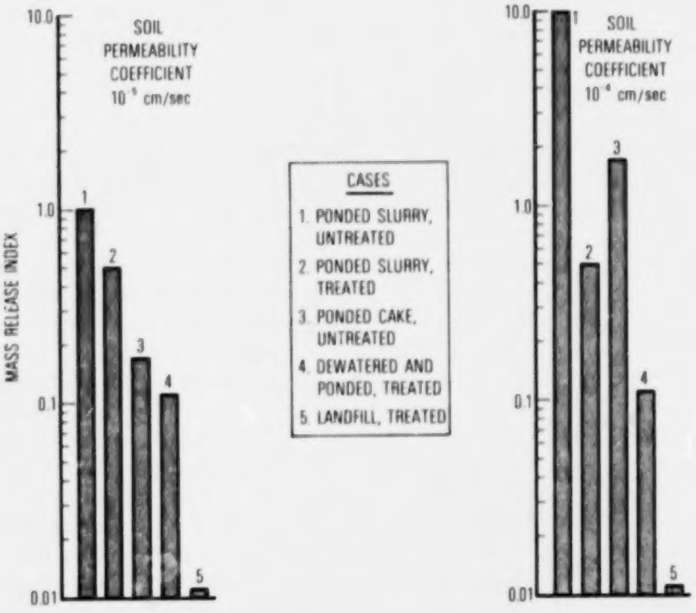


Figure 19. Comparison of mass release of sludge constituents for various disposal alternatives

In this analysis, the type of subsoil is significant for untreated sludge when the soil permeability coefficient is greater than $10^{-5}$ cm/sec. The mass release from the sludge is then directly proportional to the soil permeability coefficient (see Cases 1 and 3 for $10^{-4}$ and $10^{-5}$ cm/sec). For the treated cases (2, 4, and 5), the sludge controls seepage, and the soil does not affect the mass release from the sludge.

Case 2, Figure 19, considers chemically treated sludges disposed of in such a manner that a hydraulic head exists on the site at all times. The mass release for such a case is approximately 1/2 to 1/20 of that from an untreated slurry pond depending on subsoil permeability. Sites of this type may seep to an adjacent stream, which may reduce the concentration of constituents by mixing. Historical data regarding both the stream characteristics and water quality, as well as monitoring of streams, may be necessary before sites of this type can be considered environmentally acceptable.

## 4.2 ALTERNATIVE DISPOSAL METHOD FOR UNTREATED WASTES

The data obtained to date on the concentration of dissolved solids in the leachates of untreated sludge show that peak levels are reached which are virtually the same as those of the input sludge liquor. These concentration levels have been found to exceed drinking water criteria;[3] therefore, some form of control is needed. In addition to the use of impermeable liners or soils, one method being investigated as part of this project is the use of an underdrain system whereby the underdrained water is returned to the scrubber loop for reuse. An underdrain, vented to the atmosphere, minimizes seepage by eliminating the hydraulic head of the leachate. The gravity head of any accumulated surface water is adequate to provide for rapid removal of rainfall recharge. This technique has the potential for increasing the bearing strength of the sludge to levels useful in a landfill. This disposal operation has been investigated in laboratory tests and is currently being evaluated in the field for lime and limestone sludges and gypsum in Ponds G, F, and H, respectively. As of this writing, each has supported construction equipment, i.e., tractors and front-end loaders.

### 4.2.1 Water Balance

A water balance analysis has shown that this mode of closed-loop operation (with underdrainage water return) is possible, including the maintenance of tolerable chloride ion levels and minimum impact of fresh water makeup.[9]

In one such calculation, a 50-acre site served as a modular size for an operating disposal area, in order to capture a quantity of rainwater that would result in an acceptable underdrain to fresh water makeup ratio. (A total area of approximately 600 acres was used for a 30-foot depth of sludge, over a a 30-year plant lifetime for a 1000-MW plant, with a 50-percent average operating load factor.) The specific scrubber system chosen for the calculation was based on the TVA Shawnee venturi spray tower, using lime and extrapolated to a 1000-MW equivalent plant. A coal with 0.07-percent chlorine and an annual rainfall of 48 inches (with no evaporation) were assumed. The base case was defined as a typical closed-loop water system requiring a total of approximately 1400-gal/min fresh makeup water to replace the 900 gal/min evaporative loss via the stack and the 500 gal/min exiting the scrubber loop as occluded water in the sludge containing 45-percent solids. In the base case (nondrained), it was assumed that unevaporated rainwater supernate, was returned from the pond to the scrubber loop as makeup water.

In the study case, water that was returned from the underdrained pond to the plant reached a steady-state chloride ion concentration of approximately 5 percent greater than the base case. This represents about 5 percent of the total 1400-gal/min makeup water.

### 4.2.2 Underdrainage Seepage Rates

Characteristic drain times and seepage rates have been estimated for various sludge layer thicknesses, up to a 30-foot depth for a full-scale 50-acre pond which is filled over a five-year period. The analysis assumed quasi-steady flow through a saturated medium at rates governed by Darcy's Law. The permeability coefficients of the sludge and soil were $1.5 \times 10^{-4}$ and $2.0 \times 10^{-7}$ cm/sec, respectively. Rainfall rates consistent with those at Paducah, Kentucky, and the water balance analysis of the previous section were assumed. If an underdrain system including a one-foot thick sand layer at the sludge base is provided and vented to atmospheric pressure, no water accumulation on the surface of the pond is expected for the rainfall rate indicated at the site.

Seepage into the subsoil has been estimated assuming various hydrostatic heads at the pond subsoil interface and no interference with the natural water table. For the typical permeability coefficients used in the analysis, propagation of the leachate into the subsoil resulting from a gravity head should be approximately 1.5 feet during the five-year fill period, after which it would be covered with soil and contoured to preclude rainwater accumulation.

With no underdrain, a constant hydrostatic head at the pond-subsoil interface increases the front seepage rate significantly (Case 1, Figure 19).

### 4.2.3 Correlation of Laboratory and Field Seepage Data

The TDS concentrations in the leachate samples obtained from the chemically treated ponds approximately two years after they were filled are 45, 37, and 45 percent of the input liquor TDS for Ponds B, C, and E, respectively (Figures 16 through 18). On the basis of laboratory leaching data for cores taken from these ponds, the field TDS concentrations would represent values expected after 3, 0.5, and 2 PVDs, respectively, if the seepage at the site corresponded to test conditions in the laboratory.

Because field conditions do not duplicate laboratory cases (which is one of the major reasons for conducting a field evaluation), trends, but not exact correlations, can be derived from these comparisons. For example, laboratory conditions are closely controlled on a particular sample which may or may not be typical of the material in the vicinity of the leachate well, and the flow path through the test sample is constant. In the field, the sites which were developed over a period of a few days to a few weeks, depending on the process used, were affected during the filling by variations in sludge characteristics, chemical treatments, small scale mixing and fill procedures, and variations in the weather. Additionally, after filling, coring holes, were cut into the material, and, in Ponds B and C, a large pit was dug by the coring crew in each pond in the vicinity of the leachate wells. These holes were filled but not necessarily to the same degree of impermeability as the poured material.

Chemically treated material can develop shrinkage cracks in monolithic slabs exposed to the air during the filling process. Therefore, water entering the leachate wells in the field site could come from seepage (1) through the pores, (2) through cracks, (3) through coring holes, (4) through the two coring pits, or (5) along the sludge-pond sidewall interface. More importantly, however, an evaluation of the field leachate samples determines the quality of seepage at the lower face of the sludge, regardless of what path(s) the water takes.

An example of some comparisons that can be made using field and laboratory data is given in Table 14. The equivalent amount of seepage, in inches, through the material that has occurred in two years is indicated by Item 8 in Table 14 as 81, 10.5, and 52 inches (equivalent) for Ponds B, C, and E, respectively, and as 189 and 175 inches for the untreated materials. Since Pond B developed a seepage breakthrough in the pit dug adjacent to the leachate well and because the coefficient of permeability is approximately equal for both Ponds B and E, the equivalent seepage might be assumed the same for B as for E, i.e., 52 inches. Pond C is a more impermeable material than the other two; therefore the passage of one-fifth as much water through it as the others indicates that the sites are reacting about as expected. Another factor entering this assessment is that the subsoil is highly impermeable and generally limits the allowable seepage through the sludge (Item 11, Table 14). Therefore, because the soil limits the seepage and, in all cases but one for Pond C, the seepage appears to be greater than that allowed by the soil, it is assumed that the withdrawal of water from the leachate well is influencing a local area or areas of the ponds. To quantify actual seepage and to identify all routes and flow rates through the sludge would require multiple wells and sensing devices not amenable to the scope of this study.

It is quite possible that additional sophistication would provide a better understanding of these materials, but would not alter the conclusion that leachate from all ponds should be prevented (unless receiving waters are capable of diluting the seepage to acceptable levels) and that chemically treated disposal sites can be managed to greatly minimize or eliminate seepage to the subsoil.

## SECTION 5. DISPOSAL COST ESTIMATES

Cost estimates for ponding, chemical treatment, and landfilling have been made and reported by Aerospace on several occasions. During recent studies associated with the EPA Shawnee field disposal evaluation project, Aerospace cost estimates were made of chemical treatment disposal and were reported in the initial report on that study.[1] The Aerospace cost estimates for lined-pond disposal and chemical treatment disposal were presented in the initial report on the sludge disposal study[5] and at the EPA 1974 and 1976 Flue Gas Desulfurization Symposiums.[2,10] These estimates were updated to July 1977 costs in a more recent report.[11] A summary of the basis for the current cost estimates is presented in Table 15.

### 5.1 ECONOMICS OF DISPOSAL PROCESSES

The four FGD waste disposal methods selected for economic evaluation were as follows:

a. Ponding of untreated wastes using a flexible elastomeric liner.

b. Ponding of untreated sludges using indigenous clay pond.

## Table 14. ASSESSMENT OF LEACHATE FROM PONDS: LABORATORY AND FIELD DATA

| Item | Untreated Sludge | | Chemically Treated Sludge | | |
|---|---|---|---|---|---|
| | A | D | B | C | E |
| | Lime | Limestone | Dravo Process | IUCS Process | Chemfix Process |
| 1. Input TDS Concentration, mg/l | 8285 | 5375 | 5685 | 9530 | 6245 |
| 2. July 1976, TDS Concentration, mg/l | 4300 | 2800 | 2500 | 3500 | 2800 |
| 3. Void Fraction | 0.75[a] | 0.69[a] | 0.75 | 0.57 | 0.72 |
| 4. Sludge Coefficient of Permeability, cm/sec (typical) | $2 \times 10^{-4}$[a] | $2 \times 10^{-4}$[a] | $7 \times 10^{-5}$ | $5 \times 10^{-5}$ to $3 \times 10^{-7}$ | $2 \times 10^{-5}$ |
| 5. Pore Volume Displacement (PVD) | ≈7[a] | ≈7[a] | 3 | 0.5 | 2 |
| 6. Sludge Depth, in. | 36 | 36 | 36 | 36 | 36 |
| 7. One PVD, effective in. | 27 | 25 | 27 | 21 | 26 |
| 8. Calculated Displacement to Date, effective in. | 189 | 175 | 81 | 10.5 | 52 |
| 9. Net Precipitation, in.: Rainfall less Evaporation (12 in/yr × 2 yr) | 24 | 24 | 24 | 24 | 24 |
| 10. Calculated Seepage Based on Sludge Permeability, in. | 4960 | 4960 | 1557 | 1240 to 7.4 | 496 |
| 11. Seepage Limited by Soil Permeability in a 2-yr Period, in.: | | | | | |
| $k = 2 \times 10^{-7}$ (avg) | 5 | 5 | 5 | 5 | 5 |
| $k = 6 \times 10^{-7}$ (avg) | 15 | 15 | 15 | 15 | 15 |

[a] Reference 3.

c. Chemical treatment and landfill disposal.

d. Forced oxidation of sulfite sludge to gypsum and landfill disposal.

### 5.1.1 Ponding of Untreated Wastes

There is a number of ponding alternatives currently being used that employ flexible elastomeric liners and sites lined with indigenous clay (impervious) soil.

Since previous work[5] has shown that the optimum pond depth for this type of disposal is 30 feet, which is the depth at which pond construction and land costs are optimum with respect to the cost of liner material, the results are reported on the basis of a 30-foot depth of sludge.

Commercial materials considered typical of installed liners, i.e., PVC (20-mil thickness) and Hypalon (30-mil thickness) were used in this study. The least expensive of these two materials, i.e., PVC-20, was selected for this analysis which is summarized in Table 16. The indigenous soil is assumed to be impervious, with a permeability coefficient of $10^{-6}$ cm/sec or better.

Table 15. REFERENCE CONDITIONS FOR COST ESTIMATES

| | |
|---|---|
| Dollar Base: | July 1977 |
| Plant and Disposal Site Lifetime: | 30 yr |
| Annual Average Operating Hours: | 4380 hr/yr (30-yr avg) |
| Average Annual Capital Charges, 30-yr Average: | 18% of total capital investment |
| Cost of Land Used for Disposal: | $5000/acre, 320 acres, all land assumed purchased initially; sludge depth, 30 ft |
| Land Depreciation: | Total depreciation in 30 yr, straight line basis |
| Disposal Site: | Within one mile of the plant |
| Coal Burned: | 3.5% sulfur, 12,000 Btu/lb, 14% ash |
| Plant Characteristics: | 500 MWe, 9000 Btu/kWh (0.75-lb coal/kWh) |
| $SO_2$ Removal: | Limestone absorbent, 90% removal, 80% limestone utilization |
| Sludge Generated: | $2.5 \times 10^5$ short tons/yr (dry) (disposed waste assumed to contain 50% solids) |

Table 16. DISPOSAL COST COMPARISONS[a, b]

| Cost Basis, Mid-1977 $ | Ponding | | Landfill Chemical Treatment | Gypsum[c] |
|---|---|---|---|---|
| | Liner Added | Indigenous Clay | | |
| Mills/kWh | 1.05 | 0.70 | 1.53 | 1.40[d] |
| $/ton sludge, dry basis | 8.43 | 5.62 | 12.27 | 11.65[d] |
| $/ton coal | 2.57 | 1.70 | 3.70 | 3.55[d] |

[a] 30-year averages; 500-MW plant; 3.5% sulfur coal; 90% $SO_2$ removal.

[b] See Table 15 for all referenced conditions.

[c] 100% limestone utilization.

[d] Cost of forced oxidation and disposal of gypsum sludge (including fly ash) in an indigenous clay-lined pond.

### 5.1.2 Chemical Treatment and Disposal

The cost of chemical treatment and disposal of FGD sludge in a landfill was estimated in March 1976.[1] At that time, estimates of total disposal costs were made for three chemical treatment processes, i.e., Dravo, IU Conversion Systems, and Chemfix, for a 1000-MW plant based on 1975 dollars. With this work as a basis, cost estimates have been updated for the current conditions referenced in Table 15 and summarized in Table 16.

### 5.1.3 Economics of Conversion to Gypsum

The cost of producing gypsum as a by-product from lime or limestone 500-MWe scrubbing processes has been reported for mid-1977 by Aerospace.[9,11] The estimate included the costs required to incorporate the forced oxidation processing to a basic lime or limestone scrubber system. The fly ash was assumed to be separated in electrostatic precipitators. However, the cost of these was not charged to the cost of producing the gypsum which could be recombined later. Alternatively, the fly ash could be scrubbed in a two-stage venturi-absorber, forced oxidation system. On the basis of the power plant and scrubbing conditions shown in Table 15, $1.37 \times 10^5$ tons of ash-free gypsum (dry basis) would be produced annually.

The capital equipment costs to produce gypsum in a new 500-MWe installation, scrubbing flue gas from 3.5-percent sulfur coal, and removing 90 percent $SO_2$, is $\$6.64 \times 10^6$ or $13.28/kW. The total annual operating cost including charges on capital for this plant producing gypsum with 100-percent absorbent utilization is $\$1.52 \times 10^6$. The estimates which include the cost of oxidizing the waste to gypsum, and the disposal of the gypsum combined with 115,000 short tons of ash are summarized in Table 16.

## 5.2 COST COMPARISON

A comparison of costs for the various forms of disposal is given in Table 16. In addition to presenting the costs in mills/kWh, which are used for ease of comparison, costs are also presented in terms of cost per ton dry sludge and cost per ton coal. The disposal cost for gypsum includes the additional cost of forced oxidation of the sulfite slurry.

## SECTION 6. SUMMARY

The field evaluation project has not been completed and therefore has not yet produced final conclusions; however, the following interim findings are significant:

a. The maximum concentration of TDS in the leachate of ponds containing treated sludge occurred immediately after filling, or within a few months, and was approximately half that of the input liquors. Leachate of ponds containing untreated sludge followed a similar pattern, except the maximum concentration levels were approximately the same as the TDS of the input liquor.

   After approximately two years, the concentrations of TDS in the leachates of all ponds are between one third and one half the TDS concentrations of their respective input liquors.

b. Generally, the leachates from the evaluation ponds exhibit decreasing concentrations of chloride ion, and the TDS have stabilized at approximately gypsum saturation concentrations.

c. The groundwaters being monitored for all ponds show no effects attributable to either treated or untreated sludge disposal.

d. Chemical treatments evaluated in this project do not tend to reduce concentrations of trace elements in the sludge leachate; however, chemical treatment has been shown to minimize the release of leached sludge constituents to the subsoil through decreased permeability of the treated material and the elimination of standing water because of the amenability of the material to compaction and contouring during placement. Thus, at least a two order of magnitude reduction of mass release to the subsoil can be gained with chemically treated sludge as compared to untreated sludge. If landfill sites are properly managed, leachate seepage into the subsoil can be virtually eliminated. Laboratory results for unconfined compressive strengths of chemically treated sludges from this project have ranged ranged from 10 to 50 psi. Load-bearing strengths of chemically treated landfill materials determined in the field range from 150 to 300 psi.

e. The results of laboratory and field tests show that the load-bearing strength of untreated sludge can be significantly increased, to greater than 50 psi, if an underdrain system is used. After rewetting, underdrained sludge regains its strength within one day. A water balance analysis has shown that the mode of closed-loop operation (with underdrainage return) is possible, including the maintenance of tolerable chloride ion levels and minimal impact on fresh water makeup.

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# FULL-SCALE FGD WASTE DISPOSAL AT THE COLUMBUS AND SOUTHERN OHIO ELECTRIC'S CONESVILLE STATION

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## ABSTRACT

Conesville Generating Station, Columbus and Southern Ohio Electric Company, has recently been expanded by the addition of Unit No. 5, a 400-MW coal-fired boiler that burns 4.5 percent sulfur coal. In order to meet Ohio's New Stationary Source Performance Standard of 1.0 pounds of sulfur per million Btu, we elected to install a FGD system using thiosorbic lime that produces a sludge consisting of 30 percent solids composed of predominantly calcium sulfate and calcium sulfite.

Various alternatives for sludge disposal were investigated, including: impoundment in a strip mine area, impoundment in a nearby valley, disposal in a new lined pond adjacent to the plant site, and disposal in the existing ash pond. All of the alternatives investigated, except for the last one, were eliminated for either environmental or economic factors.

I. U. Conversion Systems (IUCS) is contracted to chemically fix the sludge to produce a stabilized material suitable for disposal. This product, known as Poz-O-Tec, will be placed in one-third of the existing ash pond. Area is available that is capable of storing the stabilized sludge for 20 years at a load factor of 51 percent.

The sludge fixation process is owned by IUCS, but is operated and maintained by Columbus and Southern Ohio Electric Company personnel. This arrangement results in a minimal capital cost, but a significantly high operating cost estimated to be 1.63 mills per kWh. This cost is expected to be reduced 0.91 mills per kWh with the operation of the No. 6 unit.

# FULL-SCALE FGD WASTE DISPOSAL AT THE COLUMBUS AND SOUTHERN OHIO ELECTRIC'S CONESVILLE STATION

## BACKGROUND

Columbus and Southern Ohio Electric Company, an investor-owned electric utility, serves over four hundred thousand customers in twenty-five counties in central and southern Ohio, with a net generating capability of over 2100 MW. Columbus and Southern operates three coal-fired steam power plants one of which is the Conesville Generating Station. Conesville is located on the Muskingum River in eastern Ohio near coal reserves owned by the Company. Conesville Station presently has a generating capability of 1625 MW with another 400 MW unit under construction. Unit #5, which was completed in 1976, is a 400 MW coal-fired unit. Unit #6 is also 400 MW and is due for start-up in March, 1978. In order to meet the existing Ohio NSPS, we elected to install an electrostatic precipitator and a lime based FGD system on each of the two units. Coal burned in Unit #5 contains 4.5% sulfur and 18% ash. The electrostatic precipitators are designed to remove 99.65% of the fly ash in the flue gas, and the FGD system, using thiosorbic lime, is designed to remove 89.7% of the sulfur dioxide. There is by-pass capability around the FGD system capable of handling up to 100% of the flue gas while the FGD system is partially or totally down for maintenance. At the present time, there is no reheat of the flue gas from this system. A portion of FGD recycle slurry containing 5% to 12% solids is bled off from the scrubbing liquor to a 145 foot diameter thickener which concentrates the slurry to approximately 30% solids;

these solids are composed of approximately 80% calcium sulfite and 20% calcium sulfate.

## STABILIZED VS. UNSTABILIZED

The production of the expected 113 tons per hour of sludge from each unit posed the obvious problem of disposal. All available information presented the sludge as a thyxotropic material which if not properly stabilized could have a deleterious effect on surface and ground waters. It was decided that fixation was required to minimize the environmental effects of the sludge in whatever manner of disposal that was chosen. Figure 1 is a ten year forecast for fuel consumed and sulfur dioxide and sludge produced by Conesville Units 5 and 6.

## DISPOSAL SITES INVESTIGATED

Economic considerations indicated that the location for sludge disposal should be near the plant site. Nearby areas that were sufficiently large enough to hold a significant quantity of sludge were investigated. Four areas were seriously considered as possible disposal sites: A strip mine area, a nearby valley, a field adjacent to the plant site, and the existing ash pond adjacent to the plant facilities.

## STRIP MINES

Ponding of the stabilized sludge in a used strip mine area located within a few miles of the plant site was studied. Disposal at this location could be with either a wet slurry or a dry stabilized sludge. Wet slurry would be conveyed by pipeline into

## FIGURE #1

## 10 YEAR FORECAST OF FUEL, SULFUR DIOXIDE, AND SLUDGE FOR CONESVILLE 5 & 6

| Year | Tons of Coal Burned | | Tons of SO2 Produced | | Tons of Dry Sludge* | |
|---|---|---|---|---|---|---|
| | Unit 5 | Unit 6 | Unit 5 | Unit 6 | Unit 5 | Unit 6 |
| 1977 | 696,000 | 0 | 61,200 | 0 | 107,000 | 0 |
| 1978 | 704,000 | 564,000 | 61,900 | 49,600 | 108,000 | 86,000 |
| 1979 | 725,000 | 737,000 | 63,800 | 64,800 | 111,000 | 113,000 |
| 1980 | 816,000 | 884,000 | 71,800 | 77,800 | 125,000 | 136,000 |
| 1981 | 675,000 | 818,000 | 59,400 | 72,000 | 104,000 | 126,000 |
| 1982 | 627,000 | 786,000 | 55,200 | 69,200 | 96,000 | 121,000 |
| 1983 | 556,000 | 699,000 | 48,900 | 61,500 | 85,000 | 107,000 |
| 1984 | 571,000 | 730,000 | 50,300 | 64,200 | 88,000 | 112,000 |
| 1985 | 520,000 | 727,000 | 45,800 | 64,000 | 80,000 | 112,000 |
| 1986 | 537,000 | 646,000 | 47,200 | 56,800 | 82,000 | 99,000 |

*Dry sludge is the underflow solids of the FGD system thickener, not the stabilized product.

interim stabilization ponds for later placement and completion; dry fixed material would be conveyed to the disposal site by conveyor belt or by truck. The physical condition of the strip mine trenches would require extensive re-grading to obtain a sealed sub-surface prior to sludge placement of the wet fixed material. The prevention of leaching chemicals into groundwater in this area was not considered feasible due to the tailings piles (random fills of soil and rock overburden) and the geological make-up of the ground. The conveying of the dry material by truck is limited to only two to three miles due to the material dewatering during hauling and causing spills on the roads to the disposal site. The installation of a conveyor belt was considered a high capital cost as well as necessitating having heavy equipment away from the plant site, where it would not be available for plant back-up in the coal yard. For these environmental and economic factors, the strip mine areas were eliminated as a reasonable placement location.

## VALLEY

Disposal of the sludge in a nearby valley behind an engineered embankment was another alternative investigated. A valley three miles from the plant site was determined capable of holding approximately 40 million cubic yards of sludge which could be stabilized in place. The sludge could be sluiced to the valley wet, conveyed on a belt conveyor, or trucked. This valley, as with almost all in this region, has been used for strip and auger mines on its interior walls. It would be necessary to seal the auger holes prior to sludge introduction to the valley. The building of an earthen dam and a pipeline for that distance posed a very large capital cost for placement of the sludge. The operation requires pumping the slurry several miles and returning the excess water back to the plant facility. The cost for this method is estimated to be between $3.60 to $4.05 per dry ton of coal. Trucking the sludge to the valley would pose the problem of sludge drippings on the county roads during transport. Conveying sludge by conveyor belts has a large capital cost. Both trucking and conveying to the valley requires heavy equipment permanently located away from the plant site which would not be available for back-up coal yard use. For these economic considerations, the valley site was not considered the best practical method available.

## POND

Consideration was given to building a pond on the land adjacent to the plant site for disposal of the stabilized scrubber sludge. One hundred and ten acres would be enclosed by earthen walls with an impervious liner covering the interior. Its close proximity to the plant would minimize transportation costs. The proposal for this site was issued to the Ohio Department of Natural Resources who, in conjunction with the U. S. Army Corps of Engineers, evaluated the request. Since the land is located in the flood plain of the Muskingum River, their joint opinion was that a loss of the flood plain would be hazardous to the community of Conesville, located across the river and just downstream of the proposed pond. The Ohio Department of Natural

Resources declared that they would not issue a permit to construct this pond for this reason.

## ON-SITE

The final alternative that was considered and ultimately selected was to divide the existing ash pond into two separate ponds; two-thirds for wet ash sluicing and one-third for stabilized sludge. The ash pond is approximately 135 acres (5,500 acre-feet) located adjacent to the power plant and receives all bottom ash and fly ash of the plant through sluice pipes. The ash pond effluent water flows into a holding pond which serves as a source for sluice water and scrubber make-up water for Unit 5 and 6. To separate the two ponds, a dike would be constructed providing 85 acres for ash disposal and 50 acres for sludge disposal. It was estimated that this would reduce the ash handling capacity from 11 years to 9years and would require an alternative ash disposal system 2 years earlier than initially calculated. It was also realized that if the sludge was produced in a dry form with load bearing capabilities, we could increase the pond capacity by building the pile above the earthen walls resulting in a mound up to 100 feet high. This volume approaches the estimated output of stabilized sludge produced by Units 5 and 6 over a 20 year period.

## IUCS CONTRACT

Disposing of the sludge in the existing ash pond appeared to be the most economically and environmentally feasible alternative. Columbus and Southern Ohio Electric Company (C&SOE) contracted I U Conversion Systems to design, engineer, construct, and manage the operation and maintenance of a fixation system to stabilize the scrubber solids into a material suitable for placement in the ash pond. The I U Conversion Systems (IUCS) contract also includes the conveyor system for placement, the supernatent return to the plant, the lighting and fencing, the sanitary system for the process facilities, and an on-site operator and maintenance training program. IUCS provides continuous resident management of the process to produce a consistent material suitable for placement. The IUCS design is required to meet all OSHA, federal, state, and EPA standards and requirements regarding air, water, noise, safety, etc. C&SOE provides the electrical power, house service water, dry fly ash, lime up to 3.5 weight percent of the sludge solids, and operating personnel. C&SOE pays IUCS an annual fee in monthly payments subject to an escalation factor.

## PROCESS DESCRIPTION

The fixation process thickens the sludge up to 60 percent solids and mixes it with fly ash and lime to produce a stabilized material labeled as Poz-O-Tec.

Underflow from the primary thickener is pumped to the stabilization system surge tank from which the slurry is then pumped to a secondary thickener, if necessary, or directly to vacuum filters. The secondary thickener was installed because preliminary data from pilot plant work indicated that the sludge could be concentrated to 40 percent solids by thickening and the vacuum filters would operate at a filtration rate of 70 pounds per square foot per hour. Testing on the actual sludge produced thus far indicates the maximum thickening capability to be approximately 36 percent solids but the filtration rate of the vacuum filters to be as high as 150 pounds per square foot per hour. The objective of either mode of operation is to operate at 60 percent solids off of the vacuum filter. The filter cake is fed into a pug mill via conveyor belt with a weigh scale to proportion the fly ash and lime feed into the same pug mill for a consistent blend of the three components. The fly ash and lime are blended first by conveying both compounds in the same screw conveyor to the pug mill. The blended mixture is conveyed outside of the process building to a radial stacker. Future plans are to locate an additional radial stacker further out in the impoundment area. It has been determined that it is more economical to construct the additional radial stacker and belt conveyors out in the impoundment area than to push the material the length of the impoundment area which is over 2000 feet.

## HANDLING THE POZ-O-TEC

The material is conveyed from the processing facility to a radial stacker where it is placed in a surge pile. The fresh material is too wet to work immediately; it is allowed to stand for 3 to 6 days to partially set-up in a manner similar to portland cement before being moved. After 3 to 6 days it is similar to clay and is manageable with the proper earth moving and handling equipment. If the material is left for more than 10 days, the pile is quite hard and breaks apart in very large boulders which hampers the movement and placement of the fixated material. Experience has shown that rubber-tired equipment has poor traction on the initially placed Poz-O-Tec. This surface condition is due to the fine grained nature of the material and the "bleeding" of surface pore water from the Poz-O-Tec when compressed during its early setting period. The film created by the bleeding effect causes the surface to be slick prior to final set. Tracked equipment, which is normally used in earth moving operations, can move the Poz-O-Tec adequately. Large, curved coal blades are not efficient in moving the Poz-O-Tec because the stabilized sludge tends to be clay-like and develops high cohesive resistence when pushed with curved coal blades designed to carry material. Smaller clay blades, which are designed to roll material forward of the blade, are better suited to push the Poz-O-Tec. The Poz-O-Tec is presently being used to build up the division dike between the sludge and ash ponds to the outer dike elevation before normal placement in the sludge pond is started. Routine disposal will consist of layers of 24 inches or less which are compacted to a dry density of 65 pounds per cubic foot.

## COST OF STABILIZATION

The cost involved in fixating the sludge is primarily an operating cost because the facility is leased. C&SOE pays IUCS an annual fee of $2,322,000, plus escalation (1976 figure). The capital costs to C&SOE involved converting the wet ash system to a dry type for the process ($1,260,000) and converting the ash pond into two separate ponds which included building a dike and relocating ash lines ($379,000). The total capital costs initially for C&SOE totalled $1,639,000 which applies to Units 5 and 6. Future expected capital costs will be for additional heavy equipment to place the fixated sludge and the costs involved in relocating the radial stacker out in the disposal area. The expected manning for Units 5 and 6's sludge fixation process and disposal is one operator per shift, 2 yardmen six days per week, and 24 man-hours per day maintenance. An estimated 10,000 tons of lime, which is equivalent to 3.3% dry solids weight, will be used to fixate the sludge for Units 5 and 6 per year. The operating cost for the process for Unit 5 alone is $2,928,000 per year or 1.63 mills per kilowatt hour. The operating cost for Units 5 and 6 combined is $3,271,000 per year or 0.91 mills per kilowatthour. Figure #2 is an itemized list of the operating costs for both Unit 5 and Units 5 and 6. Figure 3 is a comparison of fixation costs between Unit 5 and Units 5 and 6 based on several variables.

## INITIAL OPERATION

The problems encountered thus far in the fixation process fall under two categories: those of converting the plant faciliites over to the process and those of the process itself. The sludge fixation process was the last major portion of the Unit 5 and 6 facility considered in the plant design. When IUCS was contracted to build the fixation facility, the FGD system thickener was under construction as well as the wet fly

FIGURE #2

ESTIMATED OPERATING COSTS FOR UNIT 5 & UNITS 5 & 6

| Item | Unit 5* | Units 5 & 6* | Units 5 & 6 (Base Load)** |
|---|---|---|---|
| IUCS Annual Fee | $2,384,000 | $2,384,000 | $2,384,000 |
| Operating Labor | 140,000 | 140,000 | 140,000 |
| Auxiliary Power Costs | 77,000 | 115,000 | 158,000 |
| Maintenance Labor | 42,000 | 63,000 | 87,000 |
| Heavy Equipment Maintenance | 51,000 | 102,000 | 140,000 |
| Lime Usage | 234,000 | 467,000 | 641,000 |
| Total | $2,928,000 | $3,271,000 | $3,550,000 |

*These are based on a load factor of 51%
** These are based on a load factor of 70%, typical of a base load unit.

## FIGURE #3

## OPERATING COSTS FOR CHEMICAL FIXATION AND DISPOSAL

| | Unit #5* | Unit #5 & #6* | Units #5&#6 (Base Load)** |
|---|---|---|---|
| Dollars/Year | $2,928,000 | #3,271,000 | $3,550,000 |
| Mils/KWH | 1.63 | 0.91 | 0.72 |
| $/Dry Ton Sludge | 19.31 | 10.78 | 8.53 |
| $/Ton Coal | 3.85 | 2.15 | 1.70 |
| $/Dry Ton Poz-O-Tec | 11.34 | 6.33 | 5.01 |

*These are based on a load factor of 51%

**These are based on a load factor of 70%, typical of a base load unit.

ash sluicing system. It was believed that the underflow of the scrubber thickener (30 percent solids) would overload the vacuum filters of the IUCS process, so a second thickener had to be designed and installed by IUCS. IUCS requires a substantial quantity of dry fly ash (2/3 of the quantity of the dry sludge handled) for stabilizing the sludge. The fly ash conveying system had to be modified to include Nuva-feeders for pneumatic conveying to IUCS and still retain the wet sluicing option when the fly ash silos are full. The problems in the fixation process itself are all due to the use of dry fly ash. Controlling the high feed rate of the fly ash (it flows greater than 40 tons per hour) is a unique achievement that has been accomplished, thus far, only at Conesville Station. Vibrating pan feeders would not stop the flow of fly ash and many uncontrolled "floods" overflowed the equipment resulting in massive spills of fly ash inside and outside of the process building. These feeders have been replaced by screw feeders with shut-off valves and load cell flow meters to stop the flow of fly ash whenever the actual flow is measured to be greater than the set point to the screw feeders. The other major problem involves the control of fly ash dust in the process building. The dust situation is being handled by sealing the pug mills and the belt conveyors after the pug mills with a baghouse dust collection system. For each problem encountered, IUCS's effort has been to determine the source and modify the equipment and/or process to eliminate it.

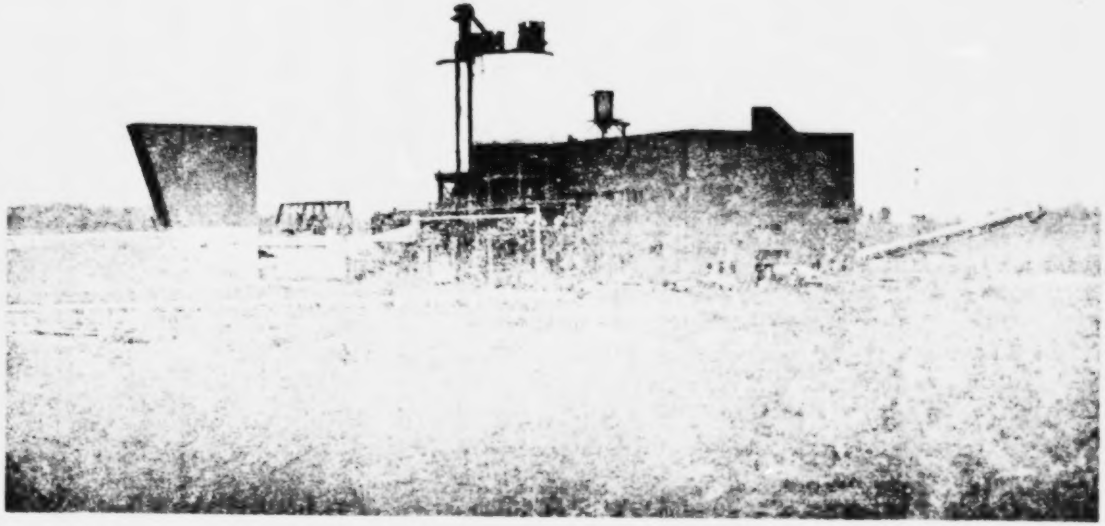
Over the last nine months, all sludge produced, (approximately 75,000 tons) has been processed into Poz-O-Tec and placed in the pond, the majority of which has been placed in the conveyor dike area.

Tests were recently conducted on in-place Poz-O-Tec material by A&H Engineering, a Columbus, Ohio based geotechnical engineering and testing firm. Preliminary results indicate that the material has developed a bearing capacity in excess of 5 tons per square foot, with an internal friction angle in excess of 45°. The physical properties of the cured Poz-O-Tec are far in excess of those normally encountered in structural earth fills, which further reinforces the capability of constructing a 100 foot mound over a 20 year period. Figures 4, 5, and 6 are pictures of the sludge stabilization building and of the sludge disposal site.

## CONCLUSION

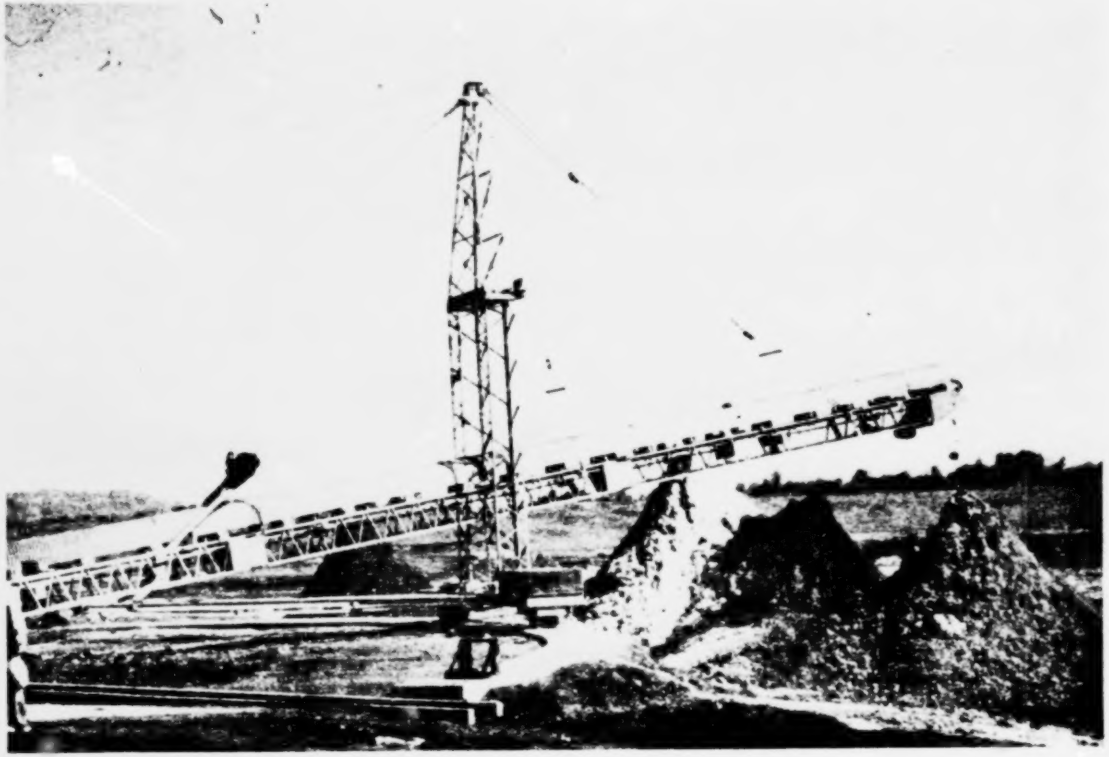
C&SOE believes that fixating of the FGD scrubber sludge with on-site disposal is the most economical and environmentally satisfactory solution for the Conesville Station. Each evaluation of disposal of FGD wastes is site specific with all possibilities considered on environmental as well as economic grounds. With less than one year's operation of the FGD system, the actual cost and operating data are only preliminary values. More informative data would be available at a later date.

FIGURE 4



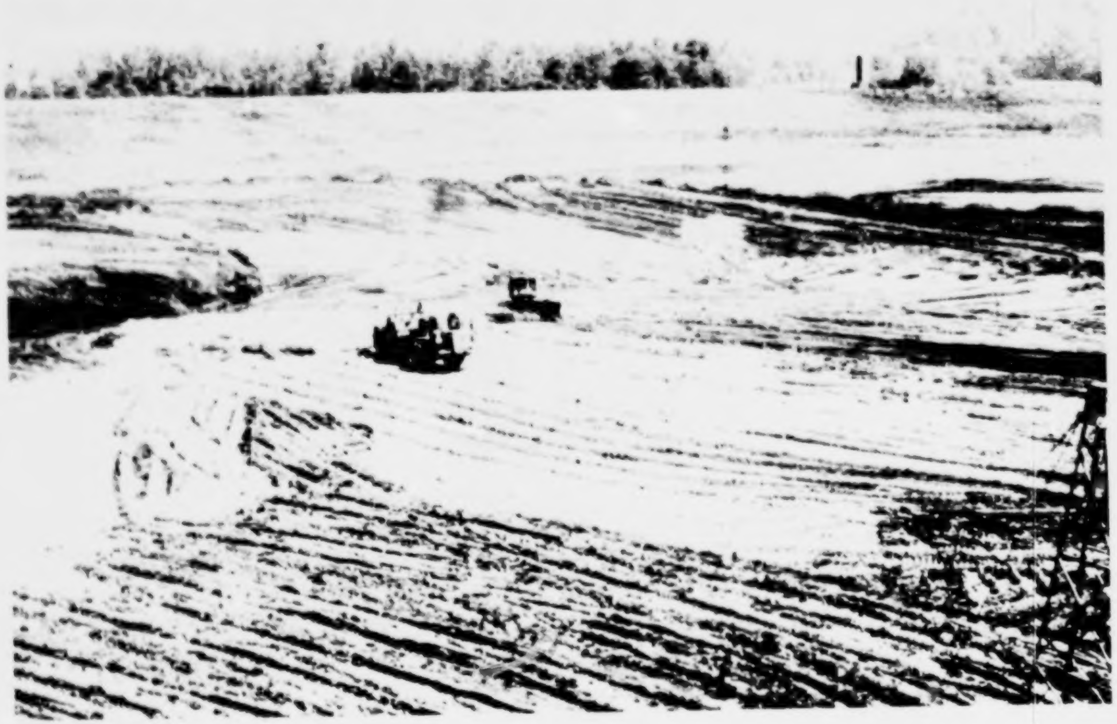
FGD SLUDGE FIXATION PLANT - CONESVILLE 5 & 6

FIGURE 5



FGD STABILIZED SLUDGE RADIAL STACKER - CONESVILLE 5 & 6

FIGURE 6



FGD STABILIZED SLUDGE DISPOSAL AREA - CONESVILLE 5 & 6

# EIGHTEEN MONTHS OF OPERATION WASTE DISPOSAL SYSTEM BRUCE MANSFIELD POWER PLANT PENNSYLVANIA POWER COMPANY

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## ABSTRACT

The Bruce Mansfield waste disposal system has been in operation since November 1975. The system is composed of four 1,000-HP positive displacement pumps, four slurry pipelines, and a 420-ft high earth and rock fill dam. Calcilox, a stabilizing additive, is supplied pneumatically to the slurry.

Operational data regarding manpower and solutions to operational problems are presented. Pump packing life has been improved by on-the-job modifications. The system is designed to act as a closed-loop system with excess water returned to the scrubbing system.

Water quality monitoring programs to meet state requirements are discussed and results presented. General maintenance requirements and operating costs are discussed.

## I. INTRODUCTION

The Bruce Mansfield waste disposal system is one of the first large scale disposal systems developed for flue gas cleaning sludge in the United States. The Bruce Mansfield station is owned by the CAPCO Group (Ohio Edison, Pennsylvania Power, Cleveland Electric and Illuminating, Duquesne Light, and Toledo Edison) and operated by Pennsylvania Power Company, a Pennsylvania - based utility. The plant is located in Shippingport, Pennsylvania, on the Ohio River approximately 35 miles downstream from Pittsburgh.

Initial construction of the plant began in 1971 with first fire scheduled for late 1975 and commercial operation of Unit I for early 1976. The plant is composed of three 825 mW net units. During initial design phases, it was anticipated existing environmental requirements could be met by "conventional" plant design philosophy, the installation of high efficiency electrostatic precipitators and a tall chimney. During initial design in 1970, the Commonwealth of Pennsylvania authorities required that flue gas scrubbing equipment be installed and operated to obtain construction and operating permits. Design, purchase, installation, and development of a flue gas desulfurization system was implemented in time for startup in the Fall of 1975.

This paper presents highlights of operation experience to date on the flue gas cleaning sludge waste disposal system. Work on the waste disposal system design began in June, 1973. Construction began in March, 1974, and initial operation in October, 1975. The system is basically composed of a pumping plant, a seven-mile slurry pipeline leading to the disposal area known as Little Blue Run Reservoir, which is created by a 400 foot high impoundment dam.

## II. DESCRIPTION OF THE SYSTEM

Table 1 presents the basic components of the mechanical portion of the system. The system is designed for Units 1 and 2 and is basically 100% redundant. The capacity of the impoundment by original design parameters is estimated to contain thirty years production of waste based on an average settled solids of 42% in the impoundment and an average 70% load factor. Environmental considerations led to the need to add a stabilizing agent, Calcilox additive, to the sludge; and at the completion of the life of the impoundment it is planned that this sludge treatment method will enable the area to be developed as a lake or as dry land. Figure 1 presents the air quality control system for the Bruce Mansfield power plant.

## TABLE 1

### PRIMARY COMPONENTS BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

### CALCILOX ADDITIVE STORAGE & HANDLING SYSTEM

| | | |
|---|---|---|
| Storage Silos | 4 each @ | 133,500 $ft.^3$, (Active 4600 tons each) |
| Day Feed Hoppers | 2 each @ | 3000 $ft.^3$, (Active 100 tons each) |
| Pneumatic Feeders | 2 each | Capacity 900 lbs/min. (648 tons/day) |
| Barge Unloading System | 1 | Capacity 100 tons/hour |
| Truck Unloading System | 1 | To each silo and feed hopper. Capacity 20 tons/hour |

### SLURRY TRANSPORT SYSTEM

| | | |
|---|---|---|
| Mix Tanks | 2 each @ | 176,000 gals. 35 ft. diameter I.D. X 35' 1" high |
| Flush Water Tanks | 2 each @ | 385,000 gals. 32 ft. diameter X 64' high. |
| Agitators | 2 each | Twin 3 blade impeller 3 blades each 112" diameter |
| Slurry Pumps | 4 each @ | 5 cylinder Positive Displacement 1200 gpm, 1100 psi, 105 rpm,<br>9 inch bore, 9 inch stroke Drive Unit - 1000 H.P.<br>4000 V AC Induction Motor Fluid Drive - 3 to 1<br>Gear Reducer - 10.9 to 1 |
| Suction Booster Pumps | 4 each @ | 120 gpm, 50 H.P., 480 Volts, 1750 rpm |
| Cooling Water Pumps | 4 each @ | 440 gpm, 20 H.P., 480 Volts, 3500 rpm |
| Service Water Pumps | 2 each @ | 170 gpm, 5 H.P. |
| High Volume Flush Water Pumps | 3 each @ | 1800 gpm, 1500 H.P., 400 Volts, 3600 rpm |
| Flush Water Supply Pumps | 3 each @ | 450 gpm, 20 H.P., 460 Volts, 1750 rpm |

## TABLE 1 (CONTINUED)

## PRIMARY COMPONENTS BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

### SLURRY TRANSPORT SYSTEM CONT.

| | | |
|---|---|---|
| Supernatant Return Pumps | 3 | 1100 gpm, 200 H.P. |
| Return Water Booster Pumps (Low-Head) | 2 | 2200 gpm 100 H.P. |
| Return Water Booster Pumps (High-Head) | 2 | 750 gpm 350 H.P. |
| River Discharge Pumps | 2 | 1800 gpm, 300 H.P. |

### ELECTRIC POWER SUPPLY

| | | |
|---|---|---|
| 13.8 Kv. Feeder | 2 | from Cranking Bus No. 1 and 1B |
| Main Circuit Breakers | 2 | 15 KV, 1200 amperes (61 KA MOM) |
| Power Transformers | 2 | 13.8 KV to 4160 V 10,000/12,500KVA 60 cycle oil filled air dried |
| 4 KV Switchgear | 1 | Bus Rated - 4160 volts, 3000 amperes (80 KA MOM) 3 phase |
| 480 Volt Power Center | 1 | Bus Rated - 480 volts, 3000 amperes (50,000 A MOM) 3 phase |
| Transfomers | 2 | 2500 KVA, 4160 volts to 480 volts 3 phase, 60 cycles |
| Reservoir Power Center | 2 | Transformer T1 23KV to 4160 Volts, 1000 KVA<br>Transformer T2 4160 v to 480 Volts, 1500 KVA |

### RESERVOIR DISPOSAL AREA

| | |
|---|---|
| Surface Area and Elevation | 1400 acre and 745 ft. to 1100 ft. |
| Capacity | Approx. 22 years at L.F. = 100%<br>or<br>30 years at L.F. = 70% |

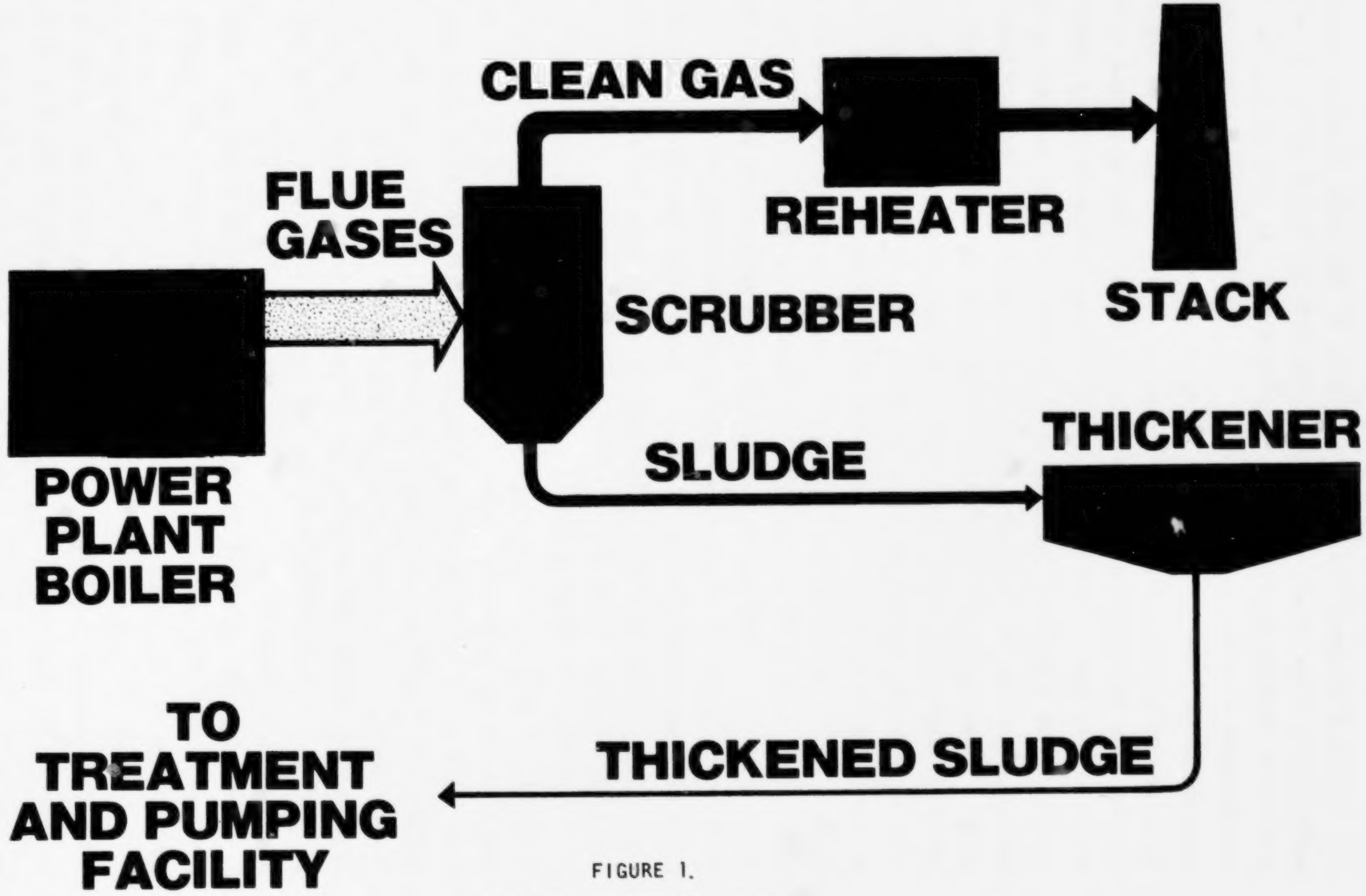


FIGURE 1.

AIR QUALITY CONTROL SYSTEM
BRUCE MANSFIELD POWER PLANT

Figure 2 presents the basic components of the waste disposal system. The waste slurry comes from the thickener underflow at 25-35% solids by weight to a mix tank located adjacent to the pumping plant. At this point, the stabilizing agent is mixed with the sludge. The retention mixing time is 20 minutes at design flow. The stabilizing agent, Calcilox additive, is delivered by barge, unloaded pneumatically into one of four 4,500 ton silos and reclaimed from the silos through a second pneumatic system and added to the sludge. A schematic of the handling and storage of the Calcilox additive facilities is shown in Figure 3. The instrumentation for determining the percent of solids consists of a magnetic Flow Meter and a Nuclear Density gauge. These signals are sent to an integrator, which in turn signals a variable speed drive vibrating screw feeder which meters the Calcilox additive into an airslide for conveying to the mix tank. After retention time and suitable mixing in the tank, the slurry additive mixture, at 25-35% solids, is taken from the bottom of the mix tank through a centrifugal rubber-lined pump which keeps a positive pressure on the main slurry pumps. Table 2 outlines the slurry and process design parameters. The main slurry pumps are manufactured by Ingersoll Rand, Aldrige Division, and described as five plunger, positive displacement, 1,000 HP pumps. These pumps operate at 1,100 psig discharge pressure at 1,200 gallons per minute to pump the slurry approximately seven miles down river to the impoundment dam.

A profile of the pipeline is given in Figure 4. The slurry lines consist of two 8 in. and two 12 in. Schedule 80 carbon steel pipes. The need for the two diameters of pipe arises from the requirement that the system is designed (see Table 3) to maintain a flow from the plant ranging from a minimum of 400 gallons per minute to a maximum of 3,600 gallons a minute. During preliminary design, sludge from a pilot plant scrubber was tested at the Colorado School of Mines and deposition velocity was determined to be on the order to two feet per second. This critical velocity led to the requirement for the two diameters of pipelines.

The pipeline system is equipped for high pressure flushing. Vent boxes are provided at high points and drain boxes at low points. The system is also equipped to be cleaned by use of pipeline pigs.

The overall system is designed to operate as a closed loop with supernatant and trapped rainfall runoff returned to the plant for re-use in the scrubber. The supernatant is returned via either one of the 8 or 12 inch

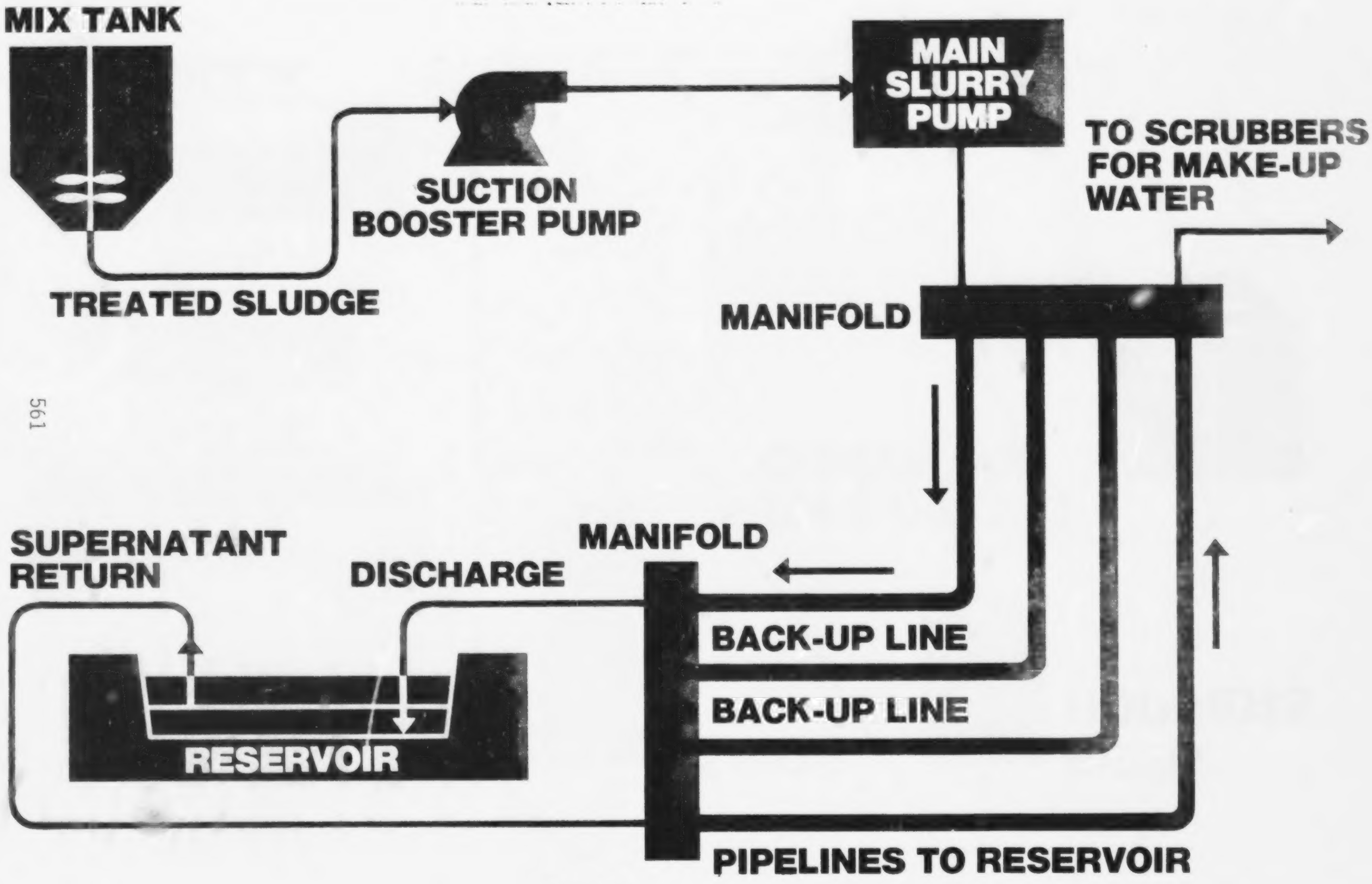


FIGURE 2.

FGC WASTE DISPOSAL SYSTEM
BRUCE MANSFIELD POWER PLANT

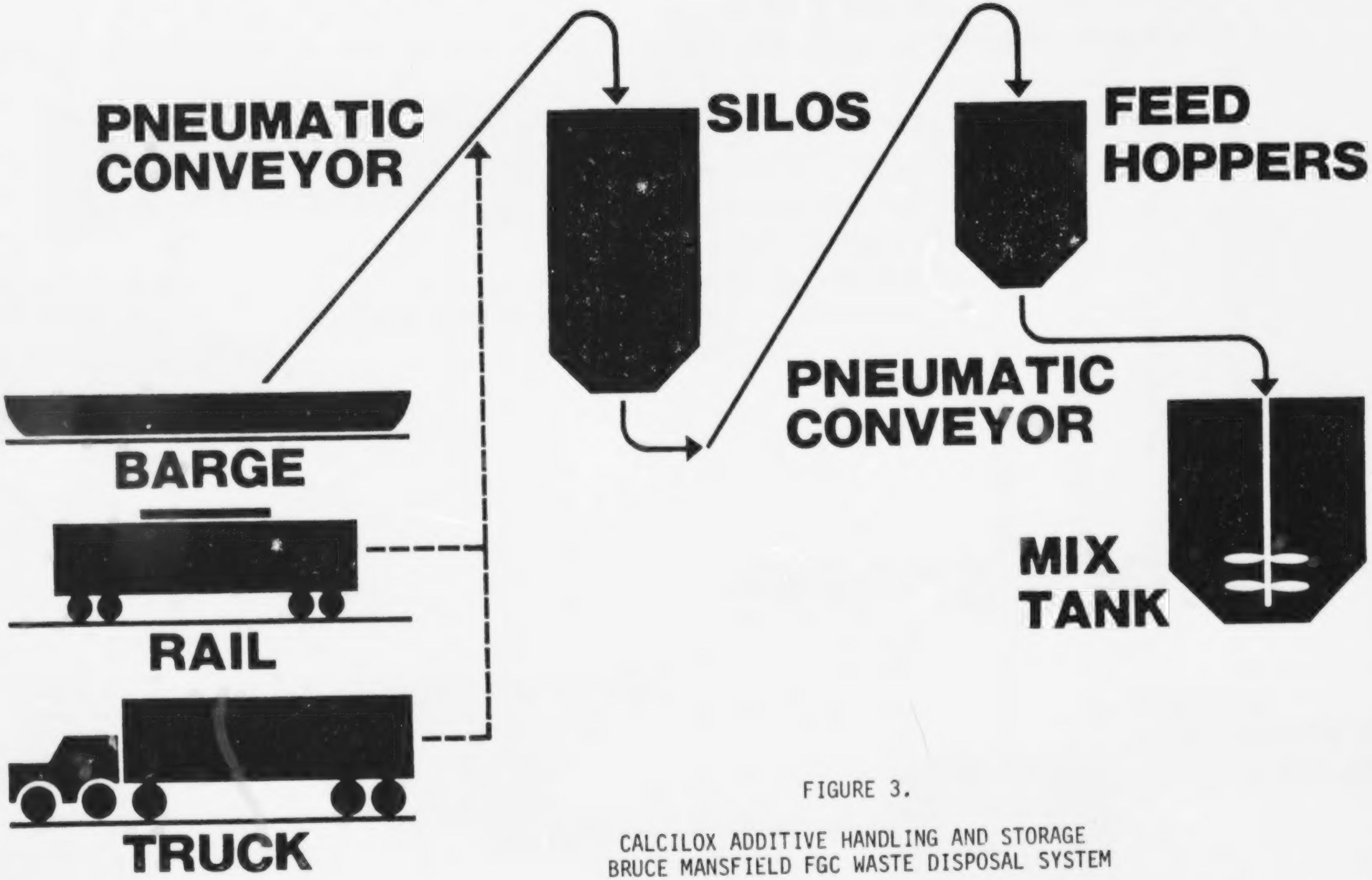


FIGURE 3.

CALCILOX ADDITIVE HANDLING AND STORAGE
BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

## TABLE 2

### SLURRY MAKE-UP PROCESS DESIGN DATA
### BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

1. THICKENER UNDERFLOW CHARACTERISTICS (before treatment)

| | |
|---|---|
| Concentration of Solids | 25% to 35% (by weight) |
| Temperature | 100°F to 125° F |
| Specific Gravity of Slurry | 1.20 to 1.29 |
| Particle Size | 250 Mesh |
| (Lime grits max. size = .25 in.) | |
| Slurry pH | 10.5 to 11 |

| Station Load | Throughput of Slurry Solids |
|---|---|
| 12.5% (25% Load Factor-one unit) | 50 TPH |
| 25.0% (25% Load Factor-two units) | 100 TPH |
| 50.0% (100% Load Factor-one unit) | 200 TPH |
| 100.0% (100% Load Factor-two units) | 400 TPH |

2. STABILIZATION TREATMENT PROCESS

| | |
|---|---|
| Calcilox additive required (at 7.5%) | 700 lbs/min |
| (504 TPD - Bulk Density = 70 pcf - S. G. = 2.75) | |
| Lime required (for pH adjustment - 1%) | 93 lbs/min |
| (67 TPD - Bulk Density = 55 pcf - S. G. = 3.30) | |

| Additive Feed Rates | Normal | Maximum |
|---|---|---|
| Calcilox additive | 7.5% | 10.0% |
| Lime | 0 | 1.0% |

Mixing Time (Minimum) 40 minutes

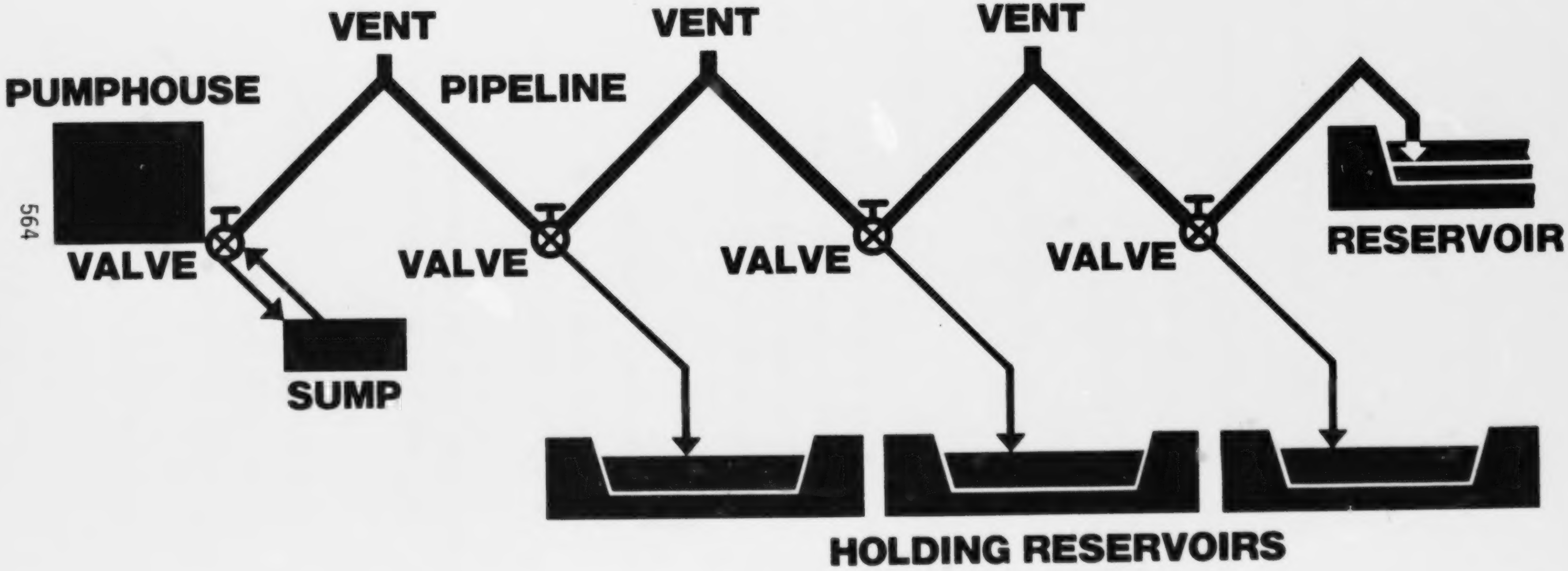


FIGURE 4.

TRANSPORT PIPELINE PROFILE
BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

## TABLE 3

## SLURRY TRANSPORT PIPELINE DESIGN DATA
## BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

Pipeline Static Head 415 ft.
(Low elev. = 725 ft. High elev. = 1140 ft.)

Friction Head Losses (Estimate) 1245 ft.

Minimum Design Flow = 400 gpm (8" pipe at 2.63 fps)
Maximum Design Flow = 3600 gpm (12" pipe at 10.18 fps)

SLURRY PUMPING CHARACTERISTICS

I. Slurry Solids = 25% Slurry Specific Gravity = 1.20

| | | Velocity | Flow Rate | Friction Head |
|---|---|---|---|---|
| 8" pipe | (Min) | 3.99 fps | 619 gpm | 32psi/mile |
| | (Max) | 7.92 fps | 1238 gpm | 92psi/mile |
| 12" pipe | (Min) | 3.54 fps | 1238 gpm | 17psi/mile |
| | (Max) | 10.18 fps | 3590 gpm | 92psi/mile |

II. Slurry Solids = 30% Slurry Specific Gravity = 1.24

| | | Velocity | Flow Rate | Friction Head |
|---|---|---|---|---|
| 8" pipe | (Min) | 3.20 fps | 500 gpm | 27psi/mile |
| | (Max) | 6.41 fps | 1000 gpm | 78psi/mile |
| 12" pipe | (Min) | 2.85 fps | 1000 gpm | 15psi/mile |
| | (Max) | 8.20 fps | 2904 gpm | 75psi/mile |

III. Slurry Solids = 35% Slurry Specific Gravity = 1.29

| | | Velocity | Flow Rate | Friction Head |
|---|---|---|---|---|
| 8" pipe | (Min) | 2.63 fps | 415 gpm | 70psi/mile |
| | (Max) | 5.21 fps | 830 gpm | 91psi/mile |
| 12" pipe | (Min) | 2.38 fps | 830 gpm | 38psi/mile |
| | (Max) | 6.78 fps | 2410 gpm | 92psi/mile |

| | | | | |
|---|---|---|---|---|
| 8" Pipeline Throughput | 46.5 TPH | to | 94.0 TPH | Slurry Solids |
| 12" Pipeline Throughput | 93.0 TPH | to | 272.0 TPH | Slurry Solids |

lines to the surge tank near the thickener and is added to the thickener overflow water. The supernatant water is pumped from the impoundment by one of three floating supernatant pumps; and should additional flow be required, booster pumps are located at the impoundment to maintain the required quantities. The system is designed to be fully automatic with control of the supernatant pumps at the reservoir linked through a telemetry system to the main pumping station at Bruce Mansfield. This system is not being operated in the automatic mode at present.

River Discharge pumps are also provided for discharge of water of suitable quality to the Ohio River. The discharge point down stream of the impoundment dam is equipped with a flow recording device and periodic samples are also taken at this point.

The impoundment area is ringed by a series of monitoring wells required by conditions of the permit granted by the Pennsylvania Department of Environmental Resources to monitor ground water quality.

A ten foot thick blanket of sand and gravel beneath the dam serves to keep pore pressures in the embankment at or near atmospheric. In addition, this drainage blanket collects seepage through the dam and around the abutments and transports this seepage to the downstream toe of the embankment. There, it is collected in a 12 inch perforated plastic pipe and discharged into the stilling basin. Monitoring of this discharge pipe has given no indication of any pollution problems. In fact, to date the records have indicated that this water is no different than the surrounding ground water.

The floating supernatant and the discharge pumps are attached by steel walkways to concrete abutments on the hillside upstream from the dam (Figure 5 ). As the reservoir and the sludge level rises, these bridges are periodically raised in 25 ft. increments.

The sludge is deposited in the reservoir through a tremie system as shown in Figure 6. The purpose of this system is to distribute the sludge uniformly throughout the 800 acre reservoir. These tremie rafts are movable and are anchored by cables to prevent wind movement. The tremie system reduced turbidity in the reservoir water and allows for uniform deposition of the stabilized sludge solids to provide uniform filling.

The 1,400 acre impoundment area initially was heavily wooded; 125 acres were cleared to elevation 900 during initial construction. It is anticipated that this will provide about three years of storage. The clearing operations

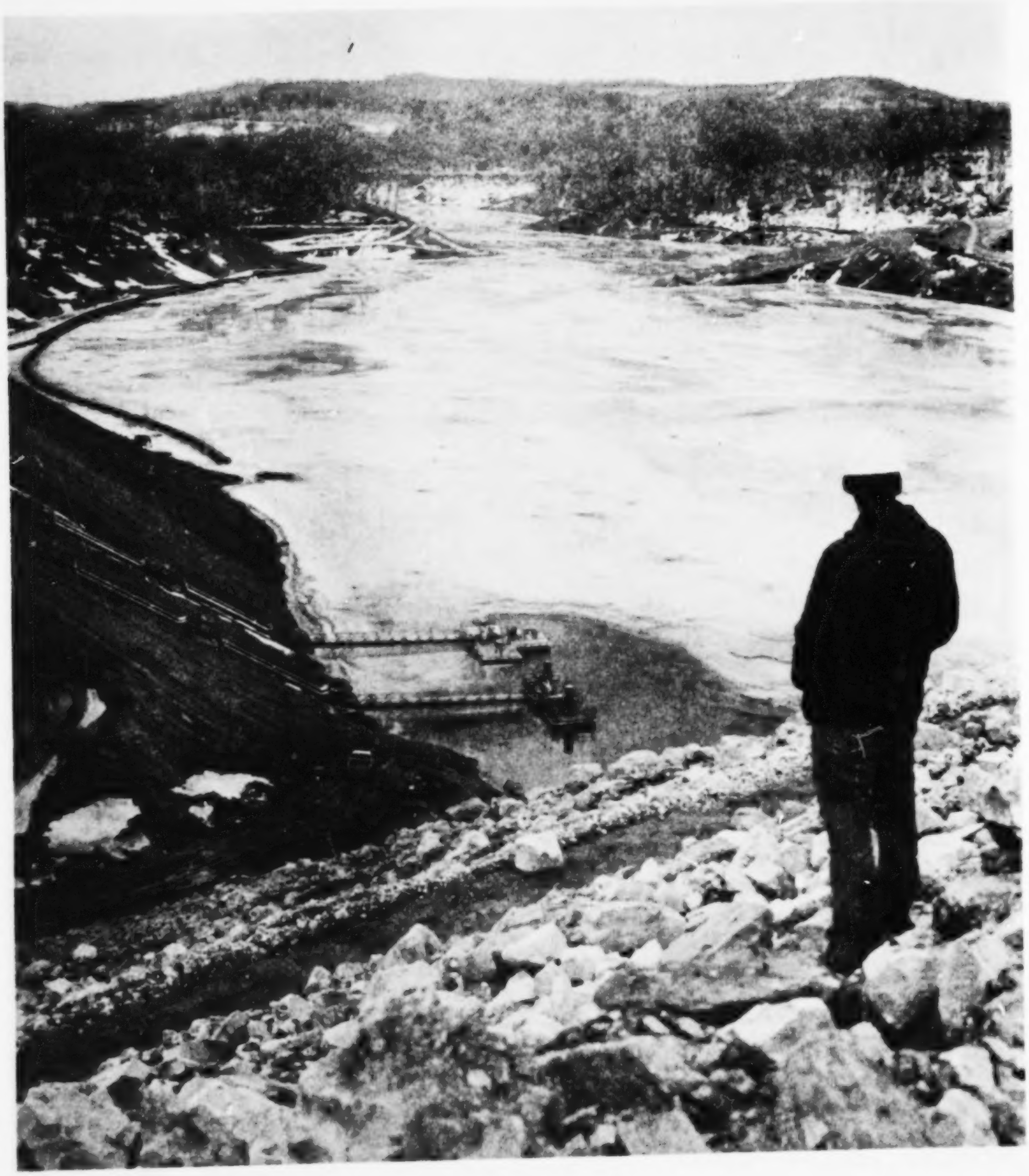


FIGURE 5. SUPERNATANT RETURN PUMPS AT LITTLE BLUE RUN RESERVOIR

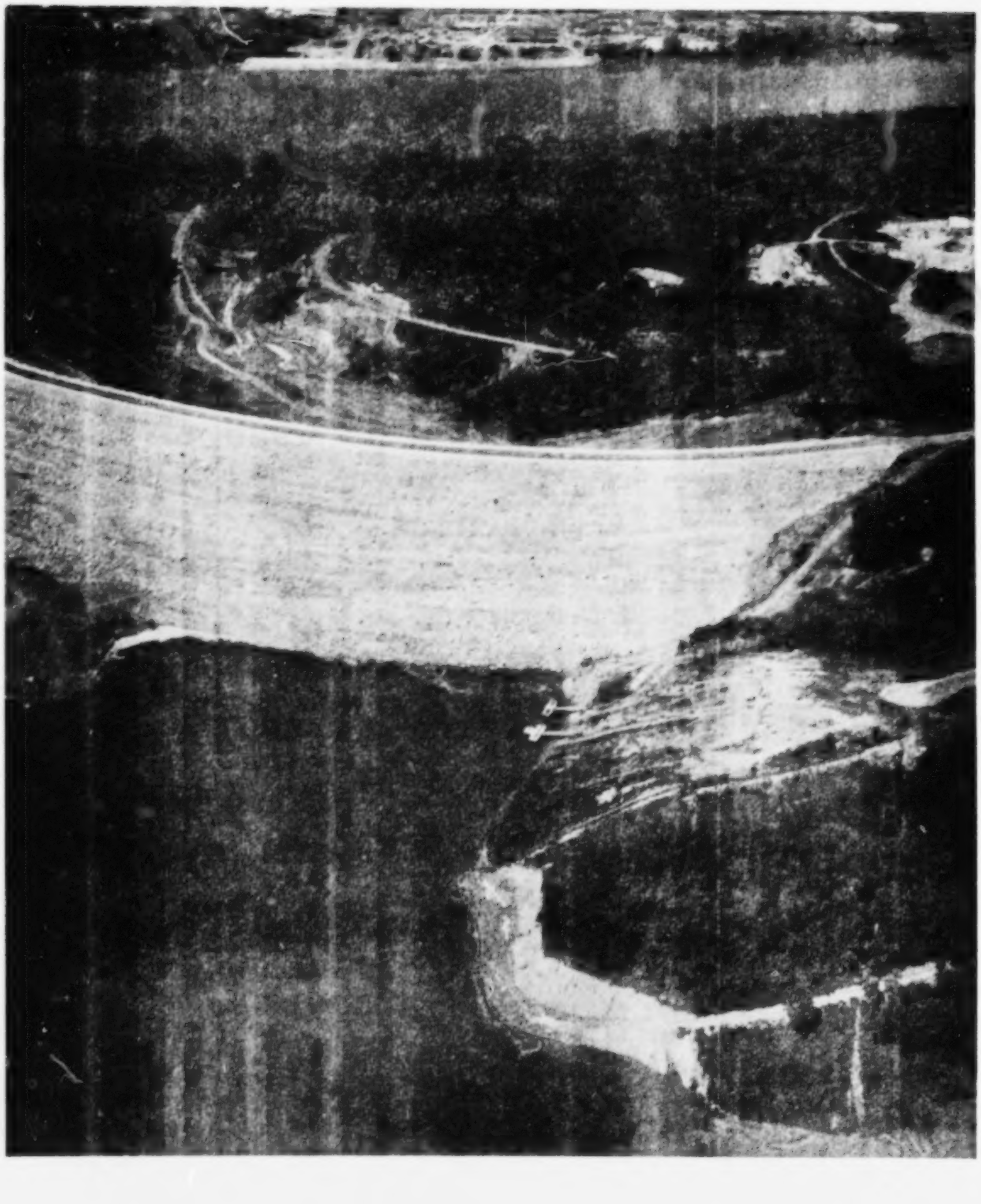


FIGURE 6. PHOTO OF FLOATING PIPELINES AND SLURRY DISCHARGE EQUIPMENT AT LITTLE BLUE RUN RESERVOIR

will continue until the end of the impoundment. Intermittent clearing provides an aesthetic surrounding for the impoundment and minimizes the impact on the animal population, allowing it to adjust slowly over the life of the development. Because supernatant was not returned to the power plant as early as originally anticipated, during the summer of 1976, it became necessary to extend clearing to elevation 950.

## III. PROJECT DEVELOPMENT

Early in the 1970's, Pennsylvania Power Company, on behalf and as agent for the CAPCO companies, began to plan and develop the Bruce Mansfield Power Plant complex as a two unit 1,650 mW project with provisions for future expansion. The target date for "first fire" in the boiler of Unit No. 1 was June 1, 1975. As a result of the regulatory requirements for installing equipment for scrubbing all of the flue gas generated, it became necessary to provide a waste disposal system as an integral part of the development. Dravo proposed application of their waste treatment process using Calcilox additive to Pennsylvania Power Company for the disposal of the resulting waste sludges.

It should be noted that a third generating unit was announced somewhat later and the requirements for complete flue gas clean-up were also imposed for this unit by the regulatory agencies. At that time, Pennsylvania Power Company determined that waste products from scrubbing Unit 3 flue gas would also be disposed of via the Unit 1 & 2 waste disposal treatment process.

Dravo's conceptual plant for waste treatment and disposal, as outlined above, was ultimately accepted by Pennsylvania Power Company and their engineer, Commonwealth Associates. During June, 1973, Pennsylvania Power Company authorized Dravo Corporation to proceed with system design and acquisition of property for the waste disposal facility for Units No. 1 and 2. To manage the project, Dravo assembled a special project team which included twenty engineers and other specialists who had full responsibility for project planning and execution.

The work of the special project team was supported by the efforts of five other organizations, each chosen for its own special expertise:

1. Gibbs and Hill, Inc. (a Dravo subsidiary) designed the overall system and detailed the slurry treatment and handling facilities.
2. Michael Baker, Jr., Inc. assumed responsibility for surveying and mapping the disposal area and for design of several required highway relocations.

3. GAI Consultants, Inc. conducted the detailed subsurface site investigation, designed the slurry retention dam and supervised the selection and placement of the embankment materials.
4. Williams Brothers Engineering Company assisted in the start-up, testing, and operational planning of the waste disposal system.
5. Thomas M. Leps, a recognized expert on earth and rock dams, was retained to assist in designing the embankment.

Slightly more than two years were available from project start to initial use. This time frame would not allow employment of the usual project sequence of detailed design, solicitation of permits, property acquisition, component procurement, construction, and start-up. In order to meet the schedule, the major project activities were carried out very nearly simultaneously.

To further clarify the project schedule, a table of major milestone dates (Table 4) and top level bar chart schedule (Figure 7) are included.

It should be noted that Dravo was given two significant advantages which assisted in the on-time completion of this project.

First, Dravo was given sole responsibility for the design and construction of the entire waste disposal package. This responsibility obligated Dravo to take the concept described earlier and transform it into a physical, working reality. However, with this responsibility Dravo was also given the authority to direct all aspects of the work and to coordinate the project working with its own personnel and with subcontractors. Adhering fully to their agreement, the client offered a maximum of cooperation and support while monitoring progress and budget closely.

Adequate authority and independence gave the contractor the opportunity to work efficiently and to advance several major activities simultaneously.

Second, use of the waste disposal system did not require completion of construction. The slurry treatment and transport equipment was specified to be 100% redundant. As long as the elements required for one flow-path were operational, the duplicate elements could still be under construction. Similarly, slurry placement in the disposal area could begin as soon as embankment height was sufficient to contain the slurry produced during the balance of construction plus the design storm. Embankment construction could be continued by working from above the water surface and from the downstream face. Initial operation was accelerated by using a manual local control panel to operate the first slurry transport pumps, thus giving the electricians unob-

### TABLE 4

### BRUCE MANSFIELD
### ACQS WASTE DISPOSAL SYSTEM

### PROJECT MILESTONES

| Date | Milestones |
|---|---|
| June 1, 1973 | Project Start |
| July 1, 1974 | Start of Construction (All Phases) |
| September 30, 1974 | Waste Disposal Permits Granted |
| November 3, 1975 | Initial Operation (Manual Mode-Basic System) |
| December 5, 1975 | Closing of the embankment |
| April 10, 1976 | Completion of the Additive Handling Systems (Main Storage Silos and Barge Dock) |
| August 1, 1976 | Completion of Pipelines |
| March 10, 1977 | First Discharge of supernatant to Ohio River, completion of discharge works |
| June 1, 1977 | Completion of the Waste Treatment System (Automatic Mode-Complete Facility) |
| July 1, 1977 | Completion of embankment |
| September 9, 1977 | Final Contractor Assistance for Operations |

Figure

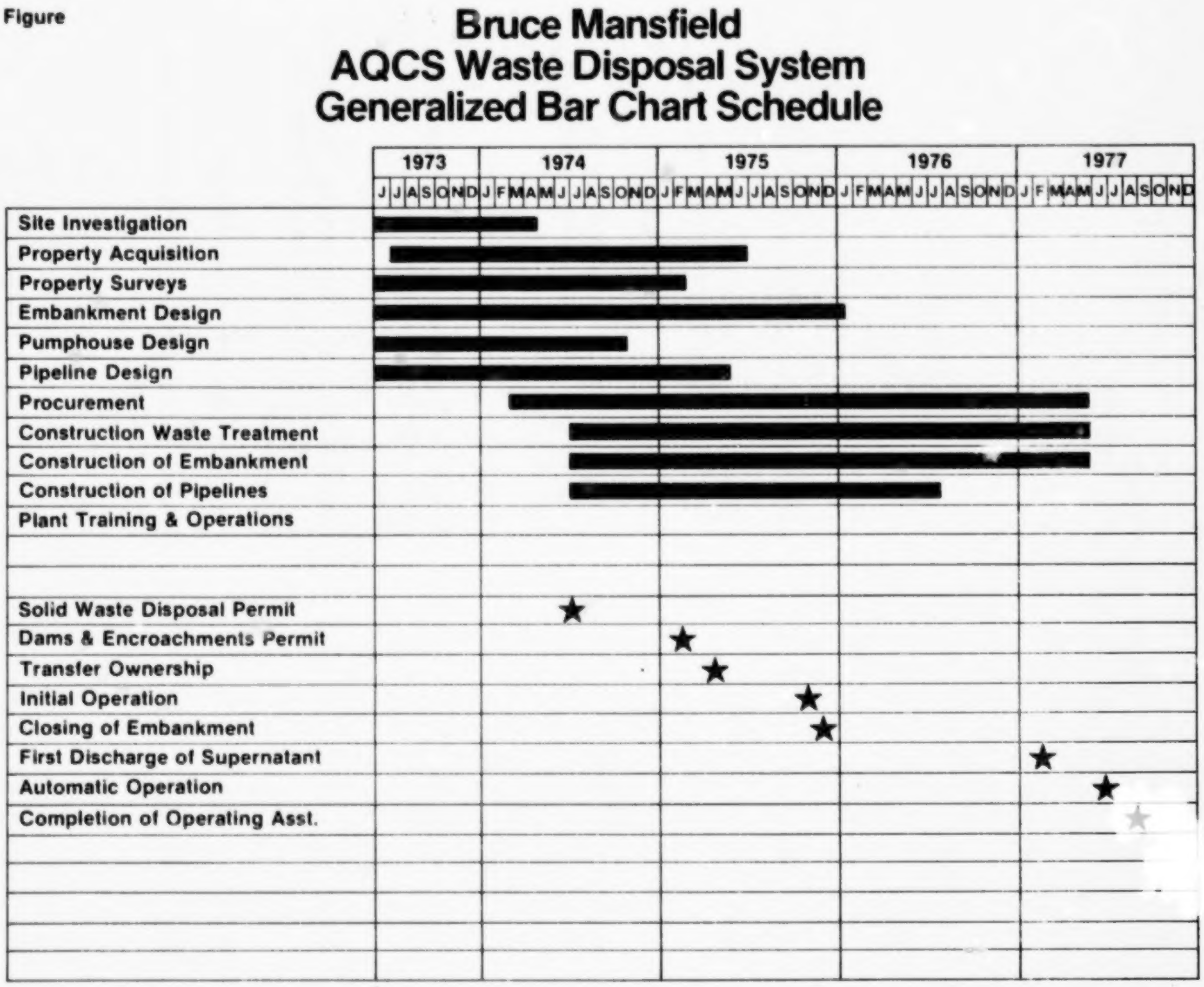


FIGURE 7.
GENERAL BAR CHART SCHEDULE

structed access to the cable ways and the automatic remote control panel (Figure 8).

Through close coordination of project activities and by aiming for achievable goals, an operating waste disposal system was complete and available for the first firing of Unit No. 1 on November 3, 1975. The minimum manual system included the following items:

- additive day storage tanks (two complete of two required)
- slurry-additive mix tanks (two/two)
- additive feed systems (two/two)
- slurry transport pump sets (two/four)
- slurry transport pipelines (one/four)
- flush water storage tanks (two/two)
- flush pumps (one/three)
- embankment completed to elevation 900. (200 ft. above the foundation).

By using the available elements, it was possible to establish a slurry flow path from the power plant to the reservoir. This flow-path, with the available back-up elements, was sufficient to maintain slurry disposal while the balance of the system was being completed over the next eighteen months.

During this eighteen month period Pennsylvania Power Company retained Dravo to provide technical assistance for start-up, operation, and maintenance of the system. While construction was being completed, a second project team was assembled to provide this required assistance and training. Technical assistance to operations was provided twenty-four hours per day for approximately nine months. This was supplemented by technical assistance for component start-up, formal operator training, and the establishment of system management procedures. As Pennsylvania Power Company developed expertise and confidence, the utility fully assumed the responsibilities of operating the system.

## IV. START-UP OF MINIMUM MANUAL SYSTEMS

Although the system is designed as a fully automatic system, lead time on the main panels, automatic controls, and much of the instrumentation was such that this equipment was not completely installed by the Fall of 1975. Start-up was accomplished by providing a temporary panel, using two sludge pumps with their associated backup systems and one 8 inch pipeline. The start-up

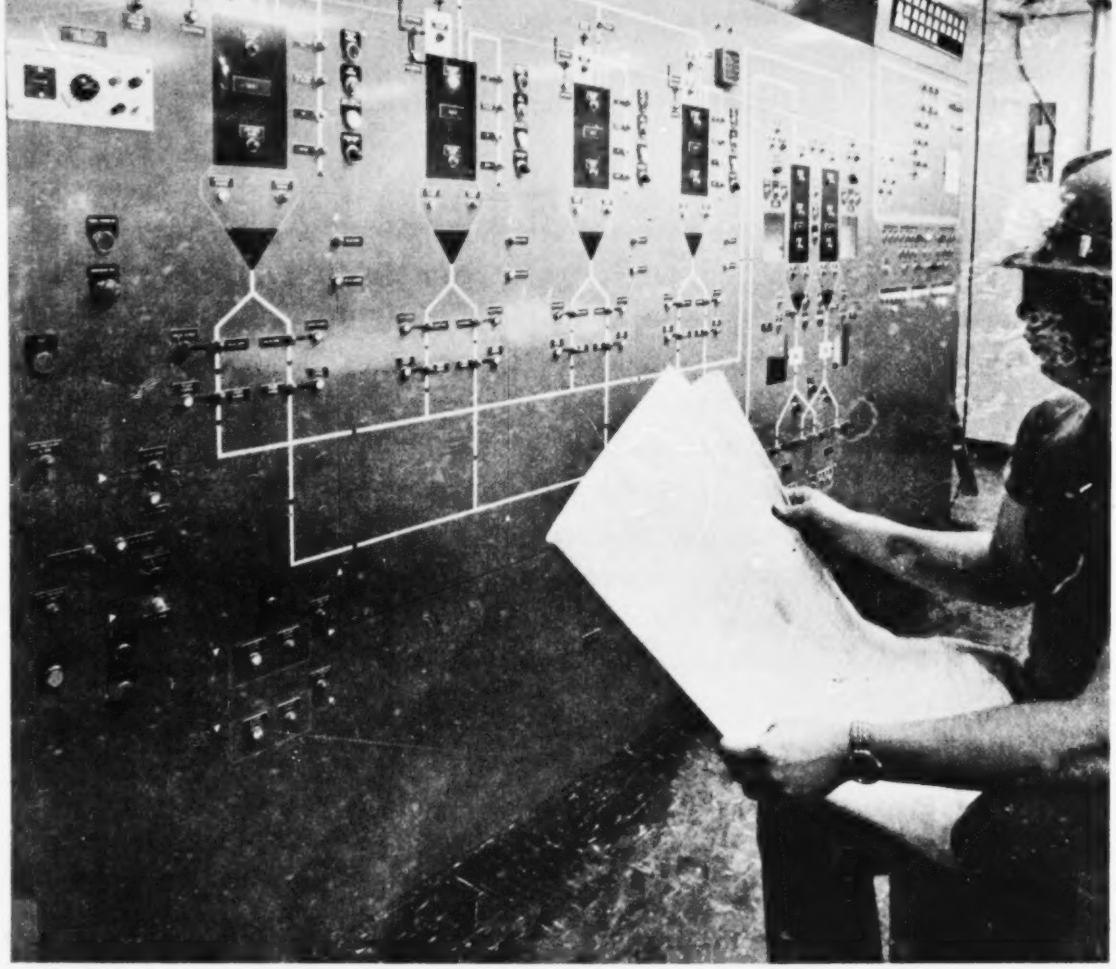


FIGURE 8. FGC WASTE TREATMENT SYSTEM CONTROL ROOM WITH PROCESS MIMIC PANELS

of the system was initiated by flooding the 8 inch line and pressure testing the system. The remainder of the lines were subsequently tested, and maximum water pressure data for various flow rates were established. These data were obtained prior to receiving any of the slurry and were used as a base line for determining operating pressures.

The system at present is fully operational in the automatic mode under Pennsylvania Power Company supervision. During 1976, operation of Unit 1 continued with two slurry pumps and one 8 inch pipeline. Flow quantities were on the order of 2,000 dry tons per day with flow rates running from 600-900 gallons per minute. During this period of time the waste disposal was operated from a temporary panel in a manual mode, and all valves were operated by hand. Again, operation of the impoundment was started before construction was completed with the dam roughly at elevation 900, 200 ft. below the final elevation of 1,100. The diversion pipe carrying Little Blue Run under the dam was plugged permanently with concrete on December 5, 1975. Pumping of slurry into the impoundment was started as of this date, and it has continued since that time. The reservoir elevation rose since December 1975 to elevation 900 in early 1977 when supernatant return to the plant was begun on an intermittent basis. Supernatant and rain water discharge to the Ohio River began in March 1977.

## V. WASTE QUANTITIES

During the initial design stage, projections of average coal characteristics, average unit load factors, and operating projections were prepared. Using this information as a basis, system design data were calculated. These data, describing the anticipated slurry and its stabilization treatment, are shown in Table 2.

Pennsylvania Power Company projects a daily, full load, average coal consumption of 8,000 tons per day per unit. This coal is projected to have a long term average sulfur content of 4.3% and a long term average ash content of 12.5%. The two-stage vertical venturi lime scrubbers, which are the core of the Bruce Mansfield Air Quality Control system, are designed to remove 99.8% of the particulate fly ash and 92.1% of the sulfur dioxide ($SO_2$) gases from the boiler flue gas prior to emission to the atmosphere. On this basis, the waste disposal system will be required to handle 6,000 tons per day (both units) of slurry solids including the additives. Assuming an average slurry solids concentration of 30%, the slurry transport system will pump 2,900 gallons per minute of slurry from the power plant to the reservoir.

As shown in Table 6, the quantity of slurry solids has been less than anticipated while the volume of waste has been much greater than anticipated. The quantities in the table are for the 22 months between November 3, 1975, and August 31, 1977. The volume of slurry solids has been less than expected because the Unit No. 1 average load factor and the average coal sulfur and ash contents have all been less than the values originally projected. However, during the same period, the total volume of waste has been substantially increased by large quantities of surplus water produced in the operation of the Unit No. 1 AQCS. Over the long term, both coal supply and power generation activities will approach a steady-state and waste quantities should average out at the original planned values.

The slurry transport system consists primarily of four high capacity pump sets each of which can be operated with any of the four pipelines. These four pump sets were started on the following dates:

| | |
|---|---|
| Pump A | November 3, 1975 |
| Pump B | November 5, 1975 |
| Pump C | February 26, 1976 |
| Pump D | December 8, 1976 |

Table 5 displays the cumulative hours of operation and the quantity of waste transported by each of the four pumps and the grand totals for the system. Table 6 breaks down the grand totals into slurry solids, including additives (weight), and quantities of thickener underflow slurry and of surplus water (volumes) which are combined to give the total of waste materials processed by the Dravo system. All of the quantities in both tables are through August 31, 1977.

For the convenience of the reader, we have also presented, in Table 5, the calculated Availability Factor for each of the four slurry transport pump sets. Availability Factor is an informal measure of pump set reliability calculated by dividing the total calendar time since initial start-up for each set into time that pumps were available for use (the sum of in-service time plus time when the pumps were out-of-service but in a fully operable condition).

At no time to date has the Waste Disposal System placed any restriction on power generation. Because of design redundancy and component reliability,

## TABLE 5

## ACCUMULATED SLURRY TRANSPORT PUMP SET OPERATING HOURS AND AVAILABILITY FACTORS

## BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

| Pump Set | Operating Hours | Availability |
|---|---|---|
| 102-A | 5879 | 94.6% |
| 102-B | 6458 | 95.8% |
| 102-C | 3688 | 83.4% |
| 102-D | 2384 | 83.7% |
| TOTALS | 18,409 | 89.4% |

Operating hours are as of August 31, 1977

## TABLE 6

## TOTAL FGC WASTE QUANTITIES PROCESSED BY THE DRAVO FACILITY AS OF AUGUST 31, 1977

### BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

| | |
|---|---|
| Total FGC Wastes Processed | 903.304,000 gallons |
| Thickener Underflow Slurry | 454,861,000 gallons |
| Thickener Underflow Solids (Dry Wt.) | 633,700 Tons |
| Surplus Water (Excess From Plant) | 525,443,000 gallons |
| Total Hours of System Operation | 18,409 hours |
| Overall Average Pumping Rate | 820GPM |

an operable waste disposal flow path has always been in service when required. All of the FGC wastes--thickener underflow and surplus water have been processed as they were released by the power plant.

It was noted above that the Bruce Mansfield Power Plant has not yet reached steady state operations. The waste disposal system continues to be confronted with atypical situations (compared to expected long term averages) which have distorted its operating results. This is mentioned to alert the reader; the results tabulated above should not be assumed to be typical of long term average quantities. It is anticipated that operating results will be reviewed on a periodic basis as the power plant operation approaches the anticipated norms. The results presented above are, however, the best data now available and are believed to be accurate indications of the situation now prevailing in the Bruce Mansfield Waste Disposal System.

## VI. OPERATING MANPOWER

Pennsylvania Power Company personnel have assumed full responsibility for all aspects of operation and maintenance of the FGC Waste Disposal System. Manpower assignments have been made on the basis of operating experience.

The Operations Department has direct control of the FGC Waste Disposal System, including housekeeping and minor maintenance. Personnel schedules are designed to provide adequate manpower at all times--24 hours per day 7 days per week. The personnel are assigned to the Waste Disposal Area on a regular, continuing basis and rotate shift assignments weekly. Three people are working in the Waste Disposal area at all times:

- one System Operator (A) who controls the system from Waste Disposal System control room
- one Assistant Operator (B) who visually monitors the system components in the pumphouse and handles inside housekeeping
- one General Helper (C) who monitors the auxiliary systems and the pipeline and handles outside housekeeping.

The direct operating manpower requires 63 manshifts per week (one man shift = eight manhours), 504 manhours per week or 26,298 manhours per year.

The operators are supervised by two people, each of whom divides his time between the Waste Disposal System and other areas. The area foreman devotes about half his time to the system, charging three manshifts or 24 hours per week (1,248 manhours per year) to Waste Disposal. Technical support is provided to the foreman by an engineer who charges about one-third of his working time (2 manshifts per week or 16 manhours per week equaling 832 manhours per year) to the system.

Major maintenance is handled by a central plant Maintenance Department which dispatches personnel on an as-needed basis from a pool of skilled craftsmen. Typically, two men are at work in the Waste Disposal Area on a one-shift per day, six day per week basis. This requires an effort of 12 man shifts per week or 4,992 manhours per year.

Additional support to the Waste Disposal Area operations comes from the Yard Department, the plant agency responsible for outdoor work and bulk materials handling. Yard personnel handle two functions for this system--the unloading of Calcilox additive from the delivery barge and the positioning of the floating segments of the slurry discharge and supernatant return pipeline. Barge deliveries are made, normally, four times per month. Unloading is done by three men in 1.5 shifts requiring a total of 36 manhours per barge or 144 manhours per month. (To date, thirty-three barge loads of Calcilox additive have been delivered, on an average of 1.5 barges per month since start-up. The actual manpower requirements to date for unloading have only been 36 manhours per month or 432 manhours per year. The difference between historic and projected deliveries is due to start-up variations and to the fact that only one unit has been in service for most of the period covered.) Positioning of the floating pipelines requires approximately 12 manshifts per month (96 manhours per month or 1,152 manhours per year). These manpower requirements are summarized in Table 7.

## VII. SYSTEM OPERATING COSTS

The cost of operating the Bruce Mansfield FGC Waste Disposal System is the total of four components: stabilizing additive costs, manpower costs, maintenance materials costs, and power costs. The historic amounts for these items over the twenty-two months covered by this report are detailed below and reduced to a cost per ton of slurry solids processed.

### Additive Costs

Between November 1975 and August 31, 1977, 32,864 tons of stabilizing additive were used to treat 633,967 tons of dry solids. This reduces to an additive cost of $1.76 per ton of dry sludge solids treated. Current de-

## TABLE 7

### FGC WASTE DISPOSAL SYSTEM MANPOWER
### REQUIREMENTS FOR OPERATIONS AND SUPPORT
### BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

| | | | |
|---|---|---|---|
| **OPERATING DEPARTMENT** | | | |
| Supervisor | 0.54 shifts/day | 6 days/week | 1,248mh/yr |
| Engineering | 0.33 shifts/day | 6 days/week | 832mh/yr |
| Operator (A) | 3 shifts/day | 7 days/week | 8,766mh/yr |
| Assistant (B) | 3 shifts/day | 7 days/week | 8,766mh/yr |
| Helper (C) | 3 shifts/day | 7 days/week | 8,766mh/yr |
| | | Sub-Total Operations | 28,378mh/yr |
| **MAINTENANCE DEPARTMENT** | | | |
| Maintenance Crew | 2 man shifts/day | 6 days/week | 4,992mh/yr |
| **YARD DEPARTMENT** | | | |
| Unloading | 4.5 manshifts/barge | 4 barges/month | 1,728mh/yr* |
| Pipelines | 12 manshifts/month | | 1,152mh/yr |
| | | Sub-Total Support | 7,872mh/yr |
| | | Grand Total | 36,250mh/yr |

*Note: Historic requirements have been less than estimated during start-up and single unit operations.

livered cost of the stabilizing additive to the Bruce Mansfield Plant is approximately $36 per ton.

## Manpower Costs

The preceding section reported the manpower requirements of the FGC Waste Disposal System operation in terms of manhours per year. These requirements are rearranged by payroll categories in Table 8. The annual manpower cost for operation and support of the system is $335,089.00.

As was noted above, the Bruce Mansfield FGC Waste Disposal System has processed 633,697 tons of slurry solids in its twenty-two months of operation (November 3, 1975 through August 31, 1977). This is equivalent to 345,650 tons of slurry solids per year. On this basis, the cost of operating and support manpower is $0.97 per dry ton of slurry solids.

## Maintenance Materials Cost

During the first eighteen months of FGC Waste Disposal System operation (November 3, 1975 to May 1, 1977) a total of $120,170.00 was expended on parts and supplies used in maintaining the facility. Through the same period 551,984 tons of slurry solids were processed by the system and transported to the disposal reservoir. The resulting maintenance material cost is $0.22 per ton of slurry solids.

## Power Costs

The Bruce Mansfield FGC Waste Disposal System is an all electric facility. To check the system's efficiency, power consumption was monitored for a 60-hour period between January 4th and 7th, 1977. The system used 207 megawatt hours of electric power during that period. The process records showed that 4,742 tons of slurry solids were treated and transported during the same period. An average power rate for a facility of this magnitude is $1.97 per kilowatt hour, net.

Doing the appropriate arithmetic gives a power cost of $0.86 per dry ton of slurry solids, which is a representative value for the operations to date.

Summary:

| | |
|---|---|
| Additive Cost | $1.76 per ton |
| Manpower Cost | 0.97 per ton |
| Maintenance Material Cost | 0.22 per ton |
| Power Cost | 0.86 per ton |
| | $3.81 per ton |

## TABLE 8

## FGC WASTE DISPOSAL SYSTEM MANPOWER COSTS FOR OPERATIONS AND SUPPORT

## BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

| Category | Pay Rate (Base & Benefits) | Manhours per Year | Cost per Year |
|---|---|---|---|
| Supervisor | 12.45 | 1248 | $15,538.00 |
| Engineer | 11.45 | 832 | 9,526.00 |
| Operator (A) | 9.70 | 8766 | 85,030.00 |
| Assistant (B) | 9.20 | 8766 | 80,647.00 |
| Helper (C) | 8.10 | 8766 | 71,004.00 |
| Mechanic (A) | 10.00 | 2496 | 24,960.00 |
| Helper (B) | 9.00 | 2496 | 22,464.00 |
| Yard (A) | 9.70 | 1440 | 13,968.00 |
| Yard (C) | 8.30 | 1440 | 11,952.00 |
| | TOTALS | 36,250 | $335,089.00 |

Based on data accumulated during the operation of the FGC Waste Disposal System for twenty-two months, the cost of processing and transporting the waste materials is \$3.81 per ton of slurry solids. This cost represents all direct operating costs; but does not include any allowances for amortization of capital or general power plant overhead.

For a number of reasons, the historic system operating cost reported here is not entirely typical of long-term costs expected for future operations. The three most prominent factors distorting unit operating costs are:

1. During start-up and shake down, the power plant has discharged quantities of excess water far in excess of those originally anticipated. Transporting this water to the disposal area has increased power and maintenance material costs without any corresponding increase in slurry solids, the basis of unit cost calculations.
2. The FGC Waste Disposal System has been designed to accommodate two 825 mW power plant units. During nearly all of the report period, only one unit has been in service. Certain of the operating costs, primarily manpower costs, are relatively fixed. Therefore, the reduction in basis of calculations increases the fixed cost portion of the total unit cost of operation. This factor has been accentuated by major interruptions in Unit No. 1 power production and by better than expected delivered coal quality leading to reduced quantities of slurry solids.
3. Despite the fact that all of the FGC Waste Disposal System components are new, reported maintenance material costs are higher than normal. The extra costs are related to materials used for minor system improvements and to learning experiences for operating and maintenance personnel.

Recognition of these factors, which have increased historic operating costs, support the conclusion that long term unit costs will be somewhat lower than those reported here. It is fair, therefore, to use the stated cost of \$3.81 per ton of slurry costs only as an upper limit on long term FGC Waste Disposal System operating costs.

The capital cost of the system is presented by the utility as approximately \$90,000,000 for Units 1 and 2. This is the total cost which includes property, the securing of permits, design, quality control, construction, and construction management. These are the costs incurred by Dravo Corporation and the utility in total. The quantity of the material to be disposed is 120,000,000 wet tons as the capacity of the Little Blue Run Reservoir. This would result in a pro-rated cost of capital as $.75 per ton.

## VIII. FULL SYSTEM OPERATION

By late fall of 1976 the system was brought into full automatic operation by moving the controls from one pump at a time from the temporary panel to the main panels in the pumphouse control room. The period from October 1975 until early March, 1977 was a hectic time in that construction and operation went on simultaneously. As a measure of the complexity of the system, there are close to 1,000,000 ft. of electrical cable with over 4,000 separate terminations and over 200 automated valves in the system. These valves had to be maintained during operation with carefully scheduled tag outs for conversion from manual mode to the automatic mode without disturbing the operation of the plant. During this period, the system availability was 100 percent.

The system is operated in conjunction with the lime slaking system. The standard manning is a supervisor and four operators on first shift, and four operators on second and third shifts. In addition to manning the lime slaking area and operating the pumping station, these operators also make a daily trip to the impoundment along the pipeline to observe the pipeline for any problem leaks, malicious mischief, or other problems. The impoundment area is also observed for proper pump operation, and general area security. In addition, the earth and rock-filled dam which creates the impoundment must be monitored on a monthly basis.

This dam is designed in accordance with the standards for any water supply dam and is instrumented to monitor any movement or buildup of water pressure internally in the dam. The data is then forwarded to the Pennsylvania Department of Environmental Resources, Division of Dam Safety.

## IX. SLUDGE STABILIZATION

The Dravo process for FGC waste treatment produces a stable, environmentally acceptable earthlike material. In the application at the Bruce Mansfield Power Plant, Pennsylvania Power Company will have the option, when the reservoir is filled, of draining off the remaining supernatant and developing the sludge bed for residential or commercial purposes or leaving the area as a lake. Proper and continuous application of the stabilization process will produce a landfill of material having a high bearing strength (unconfined compression test results frequently exceeding 4.5 TSF) and a low permeability.

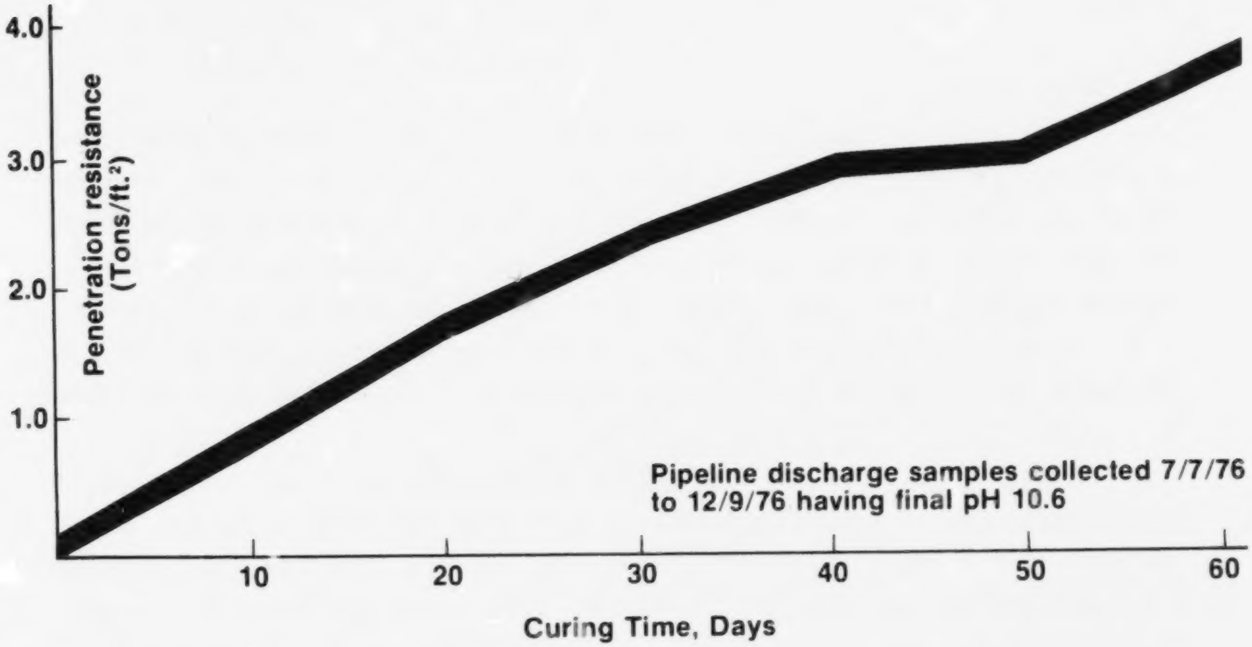
The Dravo stabilization process, as applied to the Bruce Mansfield FGC Waste Disposal System, is primarily intended for thickener underflow slurries containing 25 to 40 percent solids by weight. The most effective stabilization results when the slurry pH is controlled within the range of 10.5 to 11. This control is accomplished in this system by the addition of lime grits, with milk of lime available for further pH adjustment as required. Since the treated slurry is placed in a full impoundment, rapid stabilization is not vital and the additive feed rate is kept to a minimum. This process will produce stable sludge in sixty days or less. To certify the effectiveness of the waste stabilization process, samples of treated thickener underflow slurry have been collected daily for testing. In order to obtain samples that are most representative of the material being placed in the impoundment, the samples have been collected at the impoundment discharge of the slurry transport pipelines. These treated slurry samples are placed in wide-mouth beakers and allowed to stabilize. Periodically the condition of the sludge is checked for bearing strength (unconfined) using a pocket penetrometer. A "Soiltest" Model CL-700 penetrometer having an upper limit reading of 4.5 TSF (4.5 kg/cm$^2$) has been used throughout the test program. Devices of this type can give only approximate numerical values for unconfined compression but permit meaningful comparisons between samples and indicate the qualitative condition of each sample.

Stabilization analysis included only those pipeline discharge samples that met the process specifications - slurry solids concentration exceeding 25 percent and initial pH exceeding 10.5 - since only these samples can be considered as representative of the process. After 60 days of curing period, the pipeline discharge samples in the test group had an average penetration resistance of 3.5 tons per square foot. Figure 13 presents a graph of Average Penetration Resistance versus Curing Time for the pipeline discharge samples that met the process specifications.

Since the unconfined strength of many of the pipeline discharge samples actually exceeds the maximum penetrometer reading (4.5 TSF), Figure 9 actually understates the true average penetration resistance of the treated slurry. Therefore, this graph is a conservative representation of the effectiveness of

Figure 9.

# Average Treated Slurry Stabilization Rates Bruce Mansfield FGC Waste Disposal System



Calcilox additive as a hardening agent. To more accurately present the situation, Figure 10 is a graph showing the fraction (%) of the samples with penetration resistances exceeding 2.0 TSF versus curing time in days. Of the pipeline samples that met the stabilization process specifications, 89 percent had penetration resistances equal to or greater than 2.0 TSF after curing for 60 days.

Examination of the pipeline discharge samples supports the conclusion that the waste treatment process is effective in stabilizing these thickener underflow slurries. The results can be extrapolated to indicate that the slurry deposited in the impoundment is also stabilizing as required to form an environmentally acceptable landfill. Undisturbed samples for testing have not yet been recovered from the reservoir. Due to the great water depth over the deposit (resulting from the large quantities of surplus water discharged by the power plant) it has not yet been practical to take borings through the sludge.

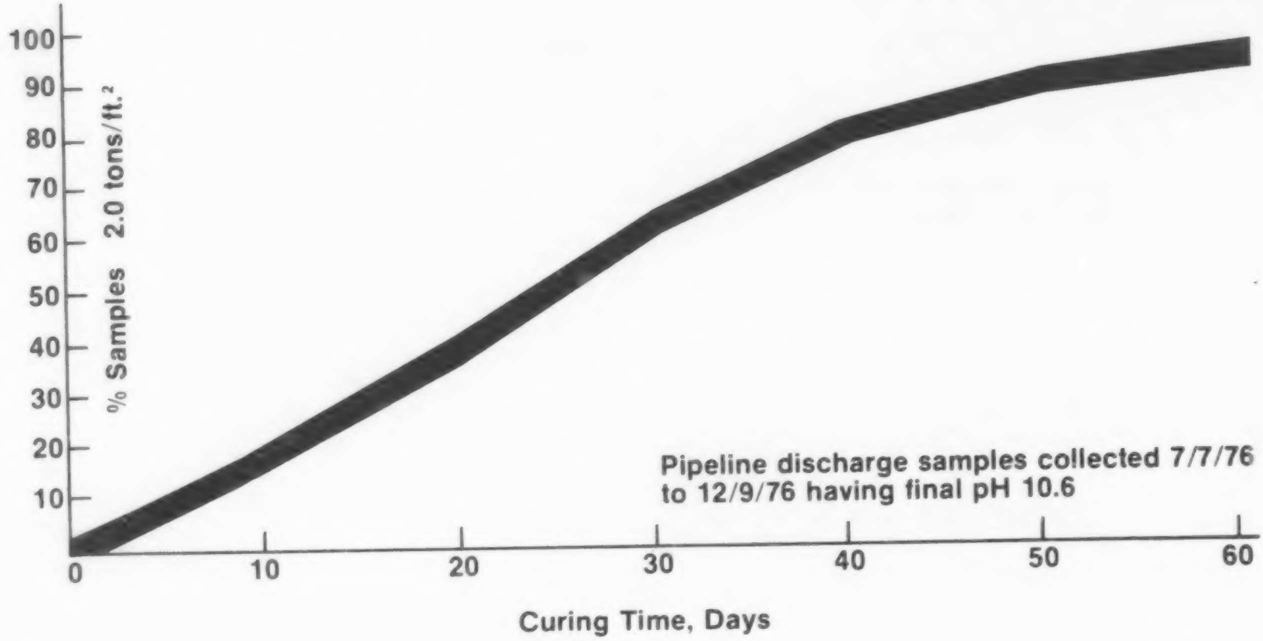
## X. WATER QUALITY

The federal and state regulations that govern the discharge of water from an industrial source into the Ohio River set limits on solids content, certain metals and water pH. Prior to the first discharge of supernatant to the March 10, 1977, reservoir water samples were collected on a weekly basis from the face of the dam, the sludge entrance area, and the upstream end of the reservoir - were checked against the limits of the river discharge permits. This discharge limits and the typical water quality test results are shown in Table 9.

In addition to the discharge quality limits shown in Table 9, the regulations also prohibit any discharge that will raise the Total Dissolved Solids content (TDS) of the river above 500 ppm. At low flow, the Ohio River carries 680 times the maximum reservoir discharge. (Ohio River low flow = 41,000 gps = 155,000 1/sec; Reservoir discharge = 60 gps = 225 1/sec.). The high Total Dissolved Solids for the river reported at the monitoring station at East Liverpool, Ohio (Mile post 40.2) during 1975/76 was 314 ppm. The highest TDS recorded during the reservoir sampling program was 2660 ppm. Dividing the total TDS mass of the combined flows by the combined flow volume gives a post-discharge river TDS at 318 ppm, well within the regulatory requirement. In fact, the addition of the reservoir discharge increases the river TDS by little more than one percent.

Figure 10.

Percentile Samples 2.0 Tons/Ft.$^2$ vs. Curing Time
Bruce Mansfield FGC Waste Disposal System



Pipeline discharge samples collected 7/7/76 to 12/9/76 having final pH 10.6

## TABLE 9

## RIVER DISCHARGE PERMIT LIMITATIONS AND LITTLE BLUE RUN RESERVOIR WATER QUALITY CHARACTERISTICS

## BRUCE MANSFIELD FGC WASTE DISPOSAL SYSTEM

| Water Quality Characteristics | Regulatory Limitations | Typical Sample Characteristics |
|---|---|---|
| Water pH | 6-9 | 7.7 |
| Total Suspended Solids (TSS) | 30 ppm (daily aver.)<br>60 ppm (maximum) | 7 ppm to 15 ppm |
| Dissolved Iron | 7.0 ppm | .1 ppm |
| Total Aluminum | 5 ppm (daily aver.)<br>10 ppm (maximum) | .2 ppm |
| Total Dissolved Solids (TDS) | 500 ppm in river flow | * |

*See Text, page 588

## XI. LESSONS LEARNED AND PROBLEMS SOLVED

This system is to our knowledge the only full scale slurry system operating where multiple pumps are manifolded into multiple pipelines with variable slurry flow, rate, and varying solids content. The traditional method of slurry pumping is a batch process. This is not practical with power plant operation, as the slurry flow is continuous varying with the plant generation load.

One of the first problems encountered was with the many valves required for system flexibility and redundancy. For efficiency of operation and to accommodate pipecleaning pigs, these are full-port ball valves. Design of all ball valves on the market at this time incorporate a cavity between the ball and the valve body. Problems were encountered with the accumulation of the sludge in the cavity of the balls and in the valve trunions. Due to this accumulation, some valves became inoperable, which reduced the redundancy and increased the maintenance cost of the system. During the summer of 1976 and early 1977, experimentation proved that by modifying the valve bodies to allow flush water pressurization of the cavity by introducing waterproof grease into the trunions and by coating the balls with the water proof grease, valve maintenance costs are significantly reduced. Some modified valves have now been in service since October, 1976, without failure.

As a result of this problem, there is presently underway a testing program for which several manufacturers have provided valves. The results of these tests are at the moment inconclusive, but some of the valves that are presently in test in the Mansfield system are full port gate valves. There are two full port gate valves, six ball valves utilizing different types of ball and seat trim. In addition, there are two plug valves which, although they cannot be put in the transfer line per se, are suitable in other applications in the system. It is expected that results from this valve testing program will probably be available in early 1978.

Another problem was associated with the Calcilox additive weigh feeders. The additive is fed gravimetrically as a percent of sludge solids into the mix tank. The original feeders were weight belt type feeders, which took a signal from the integrator and varied the belt speed to add the required amount of agent. Calcilox additive in the feeder created dust that caused belt slippage, and subsequent stoppage of the feeder. These feeders were later replaced by a vibrating screw feeder that feeds volumetrically and is controlled by a variable speed drive and an impact scale. This system has proved reliable; but periodic maintenance is required to prevent plugging and to preserve accurate calibration.

System operating experience had also shown that the sludges produced by a pilot plant are necessarily representative of those produced by a full-scale operation. The sludge produced in the pilot scrubbers showed a deposition velocity on the order of two feet per second. The sludge produced under full scale operation displays a 3.5 f.p.s. deposition velocity in the pipelines. Maintaining the pipeline velocity of the slurry above deposition velocity, is required to prevent settling of solids in the line with the potential problem of subsequent plugging. It is believed that the increase in deposition velocity is the result of the increased particle size of sludge solids produced under full scale operation. However, the system design provided sufficient flexibility to handle this change.

## XII. FUTURE DEVELOPMENT

Unit 2 began initial operation in July of 1977. Since that time two of the main slurry pumps have been in continuous operation. To date, system reliability has been 100 percent with two unit operation.

Unit 3 is scheduled to begin operation in 1980. It is anticipated that observations of the system will continue, and that a decision will be made as to whether additional slurry pumping units will be required to handle the Unit 3 load.

# MINE DISPOSAL OF FGD WASTE

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## ABSTRACT

There is substantial capacity for placement of FGD waste in mines in the U.S.. To be technically viable, mines must meet operational criteria of capacity, location, and accessibility. Environmental acceptability must be assessed on a site-specific basis. This paper discusses the principal potential impact issues requiring evaluation during mine site selection, including groundwater contamination, surface water contamination, sludge stability/consolidation and fugitive air emission. Impact issues of both underground and surface coal mines are discussed relative to the handling and placement techniques considered technically feasible.

# MINE DISPOSAL OF FGD WASTE

## 1. Introduction

Of principal concern with the widespread application of nonregenerable flue gas desulfurization FGD systems is the disposal of the large quantities of waste produced. Most utility installations of nonregenerable FGD systems now in operation in the United States employ disposal methods involving some form of on-site ponding or impoundment of the waste produced. Such ponds or impoundments require large tracts of land that may not be readily available. Depending on the sulfur content (and ash content) of the coal, the land requirement for disposal can range from 0.2 acre-feet/megawatt-year to over 1.0 acre-feet/megawatt-year. Arthur D. Little, Inc., is now conducting a study for the Industrial Environmental Research Laboratories of the U.S. Environmental Protection Agency (under Contract No. 68-03-2334) to evaluate the feasibility of using mines and the ocean as alternate sites to ponds and landfills for the disposal of FGD waste. This study involves three phases of effort:

- Phase I - Form an initial assessment of the technical, environmental, regulatory, and economic aspects of the disposal of FGD waste in mines and in the ocean, identifying key issues and defining the most feasible disposal options.
- Phase II - Gather and develop additional information related to the key issues identified in Phase I for use in preparing a refined assessment of the various disposal options and in planning and implementing laboratory and field testing in Phase III.
- Phase III - Conduct simulation and/or demonstration testing of promising ocean and mine disposal options.

Phase I has been completed, and a report was issued in May 1977 (EPA-600/7-77-051 and NTIS PB269 270/AS). Phase II has also been completed and a report is being written. Phase III has begun and is expected to continue for two years.

This paper discusses the prospects for disposing FGD waste in mines based on the initial and refined assessments performed in Phases I and II. The focus of our effort has been on the environmental effects of waste disposal, because that serves as the basis for developing disposal criteria, defining and evaluating relevant technology, formulating conceptual disposal scenarios, and assessing the adequacy of existing regulations for protecting the environment.

The overall assessment approach has been a three-step process involving:

- grouping of disposal sites by characteristic conditions and/or regions (Western versus Eastern mines, strip versus deep mines, etc.);

- evaluation of the impact of untreated waste for an assumed simple disposal operation; and

- evaluation of the effects of controlling the disposal by limiting or altering waste properties, adjusting the method of placement, or imposing indirect measures to minimize impacts.

## 2. Capacity and Technology Available for Waste Disposal

There are currently over 15,000 mines throughout the United States which together produce over 0.5 billion tons of coal and 2.5 billion tons of metallic and nonmetallic minerals each year. About one-third of the mines individually produce over 100,000 tons annually. Such mines represent an enormous capacity for the disposal of waste materials.

However, much of the capacity is clearly not suitable for FGD waste disposal. The method of mining, for example, can preclude practical waste disposal operations. Underground mining which employs caving or cut-and-fill techniques leave little available void for waste disposal. In open-pit mining, overburden is often removed from the mine area and the mineral is mined downward from the surface in benches, or the mining operation may follow the ore strata downdip from its surface outcrop, which requires that the area mined be left open for access of haulage vehicles.

Four mine types provide the greatest potential for disposal of large quantities of FGD waste in terms of overall technical feasibility:

- surface coal mines,

- underground room-and-pillar coal mines,

- underground room-and-pillar limestone mines, and

- underground room-and-pillar lead/zinc mines.

This selection is based on considerations of capacity for waste, ease of disposal, prevention of future resource recovery, and general proximity to waste sources. This screening of mines was derived from a national perspective to focus on mine categories of greatest significance, so it does not consider small mines that have site-specific conditions favorable to waste disposal.

Coal mines are the most likely candidates for waste disposal. They offer the greatest capacity for disposal and are frequently tied directly to power plants. This paper will focus on the use of coal mines; however, the impacts and overall viability of disposal operations would be expected to be generally the same for similar mining methods and environments.

In 1976, over 665 million tons of coal were mined in the United States. About half of the coal was produced from underground mines and half in surface mines. Figure 1 shows the approximate distribution of coal mined for utility consumption by region and mining method. (By contrast, the total combined production from limestone and lead/zinc mines amounts to less than 10% of the total annual coal production.) Table 1 shows the 1973 distribution of coal mines by region and mining method. Of the total coal produced, over 450 million tons of coal were mined for use in utility boilers.

Depending upon the type of coal, FGD system, and emission standards to be met, the volume of ash-free waste (50% solids) can range from less than 5% to almost 30% of the volume of coal burned. However, the volume of coal mined is not necessarily the volume of the available void space for disposal. For active surface mines and underground room-and-pillar mines waste disposal would have to be scheduled to keep up with the continuous extraction/reclamation process. This would not be a problem if the waste produced from the coal at any particular mine were returned for disposal. In underground mines, increased use of pillar robbing and long-wall mining techniques allows roof collapse to fill a significant fraction of the void and renders other void areas inaccessible.

The methods used in disposing of FGD waste in mines must be compatible with the mining operation at each site. The placement and handling techniques for disposal of FGD waste are available and demonstrated for storing other materials in mines, although methods may require some modification for application to FGD waste.

In surface mines there are basically three options for waste placement:

- in the working pit, following coal extraction and prior to return of overburden;
- in the spoil banks, after return of the overburden but prior to final reclamation of the land; and
- mixed with or sandwiched between layers of overburden.

Figure 2 illustrates typical operations in surface area strip mines. Figure 3 illustrates typical operations in contour strip mining. Truck dumping, such as that used for returning coal refuse, would be the easiest and possibly the only practical method of placement. In an active mine, truck dumping in the pit is probably the most attractive option, because it can be accomplished without construction of additional roads or accessways.

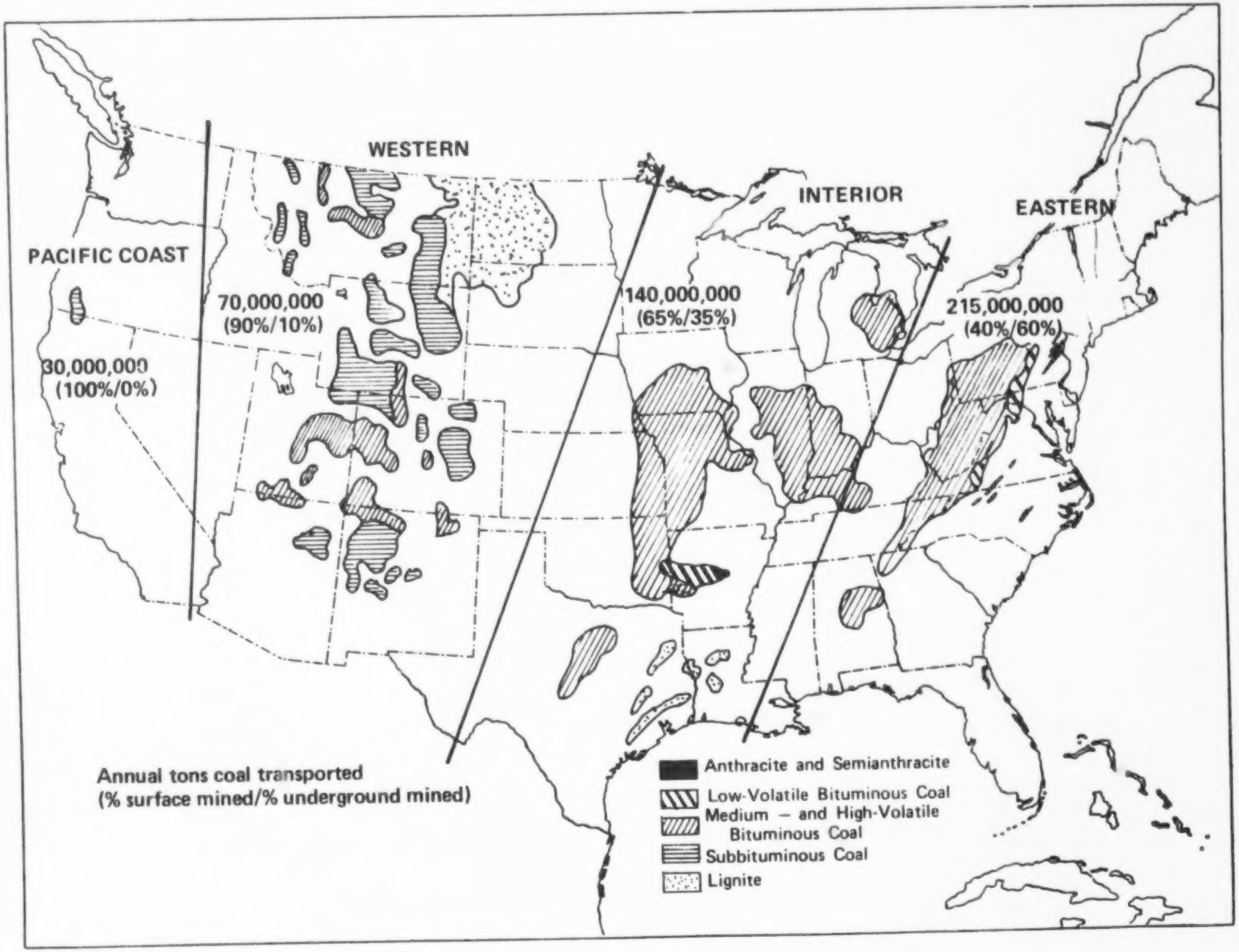

WESTERN
INTERIOR
EASTERN
PACIFIC COAST
70,000,000
(90%/10%)
140,000,000
(65%/35%)
215,000,000
(40%/60%)
30,000,000
(100%/0%)
Annual tons coal transported
(% surface mined/% underground mined)
■ Anthracite and Semianthracite
▨ Low-Volatile Bituminous Coal
▨ Medium – and High-Volatile Bituminous Coal
▤ Subbituminous Coal
░ Lignite

FIGURE 1 COAL PRODUCTION FOR UTILITY POWER PLANT USE (1976)

## TABLE 1

## COAL MINING DISTRIBUTION BY REGION (1973)

| | Total % of Production | | | Number of Mines | | |
|---|---|---|---|---|---|---|
| Region | Surface | Underground | Total | Surface | Underground | Total |
| Eastern | 23.7 | 39.9 | 63.6 | 332 | 248 | 580 |
| Interior | 17.1 | 9.4 | 26.5 | 53 | 23 | 76 |
| Western | 7.5 | 1.7 | 9.2 | 28 | 10 | 38 |
| Pacific | 0.7 | < 0.1 | 0.7 | 2 | 1 | 3 |
| TOTAL | 49.0 | 51.0 | 100.0 | 415 | 282 | 697 |

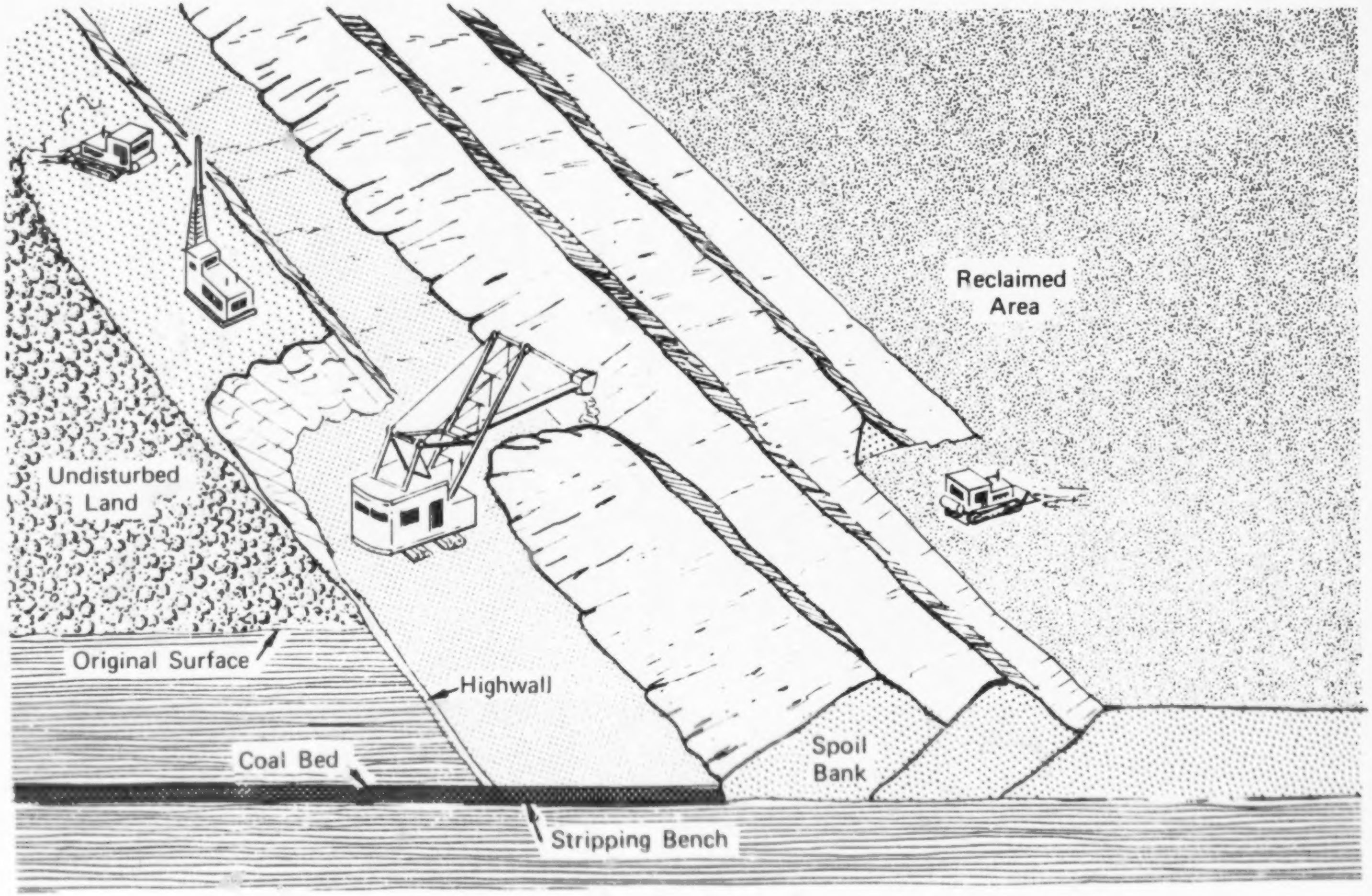
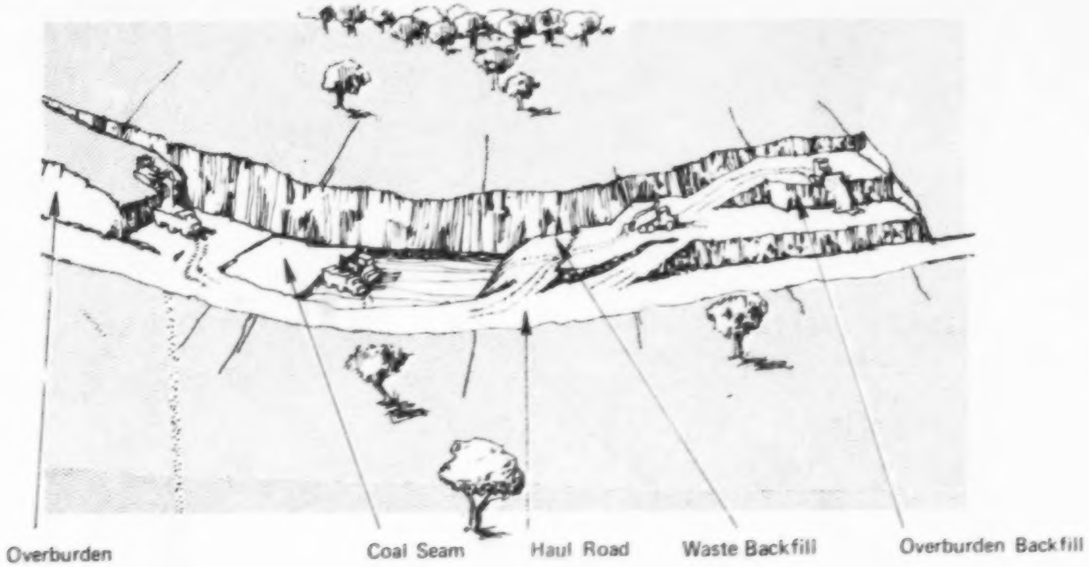


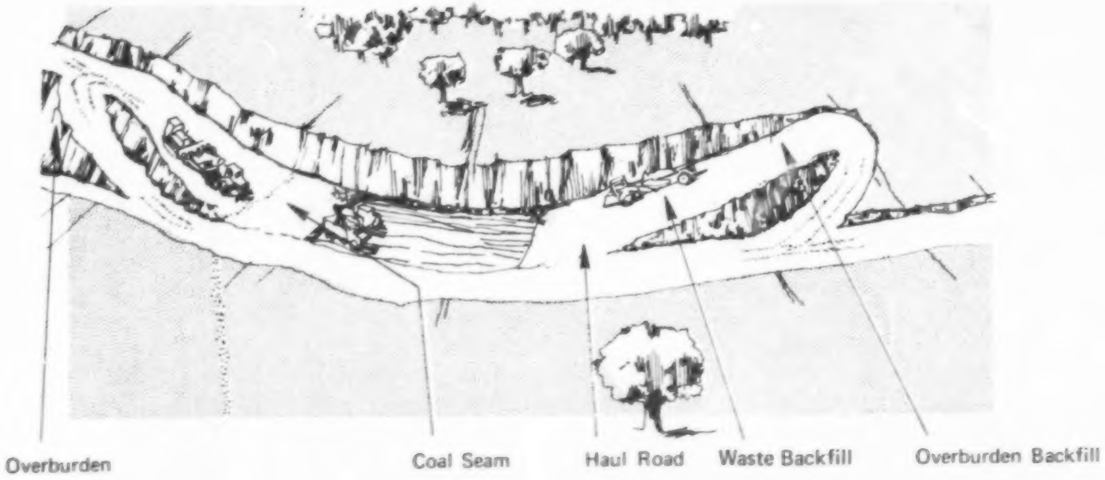
FIGURE 2 AREA STRIP MINING WITH CONCURRENT RECLAMATION

# BLOCK METHODS OF CONTOUR STRIP MINING

The Truck Haulback Method



The Scraper Haulback Method



However, for any of the options, the waste must be relatively dry, and disposal operations must be scheduled to cause minimal disruption of mining operations.

In underground room-and-pillar mines, where the available disposal space is downdip of the active mining area, waste can be placed either as a slurry through hydraulic backfilling or it can be mechanically stowed as a dry material. Hydraulic backfilling has been used for stowing in metal mines (where sandfill is a part of the mining operation) and for disposing of fly ash in coal mines. If hydraulic backfilling is used, bulkheads would probably need to be constructed between pillars, and the waste pumped through boreholes drilled from the ground surface to the available mine void. Figure 4 illustrates hydraulic backfill operations in an underground room-and-pillar mine. In underground longwall mining (where the roof is collapsed into the mine void), and in underground room-and-pillar mines where the available space for waste disposal is updip of the active mining operation, dry waste can be placed either by mechanical or pneumatic stowing. Coal refuse has been placed by pneumatic means in some European underground room-and-pillar mines.

## 3. Waste Characteristics

### (a) Chemical Properties

Both the chemical composition and the physical and engineering properties of the waste produced by any FGD system at any particular time will depend upon a variety of factors including:

- composition of the coal burned;
- type of boiler and its operating conditions;
- method of particulate control employed; and
- type of FGD system and the way in which it is operated.

Thus, waste characteristics and chemical composition can vary over extremely wide ranges.

The principal substances making up the solid phase of FGD waste are calcium-sulfur salts (calcium sulfite and/or calcium sulfate) along with varying amounts of calcium carbonate, unreacted lime, inerts and/or fly ash. The ratio of calcium sulfite to calcium sulfate (present as $CaSO_4 \cdot 1/2\ H_2O$ or gypsum, $CaSO_4 \cdot 2H_2O$) will depend principally on the extent to which oxidation occurs within the system. Oxidation is generally highest in systems installed on boilers burning low sulfur coal or in systems where oxidation is intentionally promoted. Fly ash will be a principal constituent of waste only if the scrubber serves as a particulate control device in addition to $SO_2$ removal, or if separately collected fly ash is admixed with

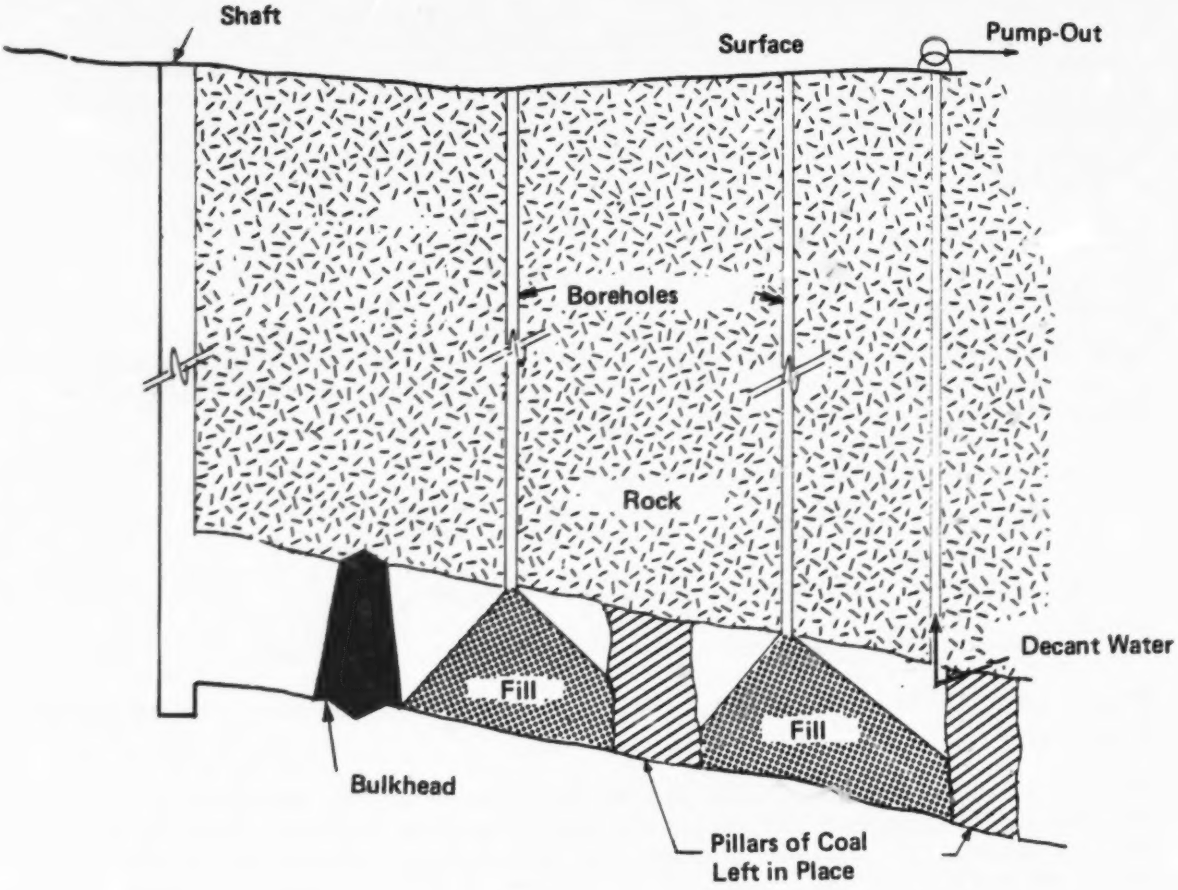


FIGURE 4 HYDRAULIC BACKFILLING OF WORKED OUT PORTION OF A ROOM-AND-PILLAR COAL MINE

waste. The amount of inerts and unreacted raw materials (lime and/or limestone) in wastes will depend upon the quality and utilization of raw materials (system stoichiometry).

A variety of trace elements find their way into FGD wastes from a number of sources: from coal where they are present either in mineral impurities or as organometallic compounds; from lime, limestone, or other reagents used in FGD wastes; and even from the process water makeup used. The greatest source of trace elements, though, is from the coal fired, and the levels of trace elements depend primarily on their level in the coal, the amount, if any, of ash that is collected or admixed with the wastes and the efficiency of the scrubber system in capturing trace metal vapors and fine particulate. Most of the elements in coal are not highly volatile and will be retained in the ash matrix (either as fly ash or bottom ash). The concentrations in the waste of those elements that are most highly volatile (notably arsenic, mercury, selenium, beryllium, chloride, and fluoride) will depend on the extent to which they are present and released from the coal, and more importantly, the efficiency with which they are captured in the scrubber. Mercury and selenium are likely to be present in the flue gas as elemental vapors that might not be scrubbed efficiently; chloride and fluoride are almost completely released from the coal and are very efficiently scrubbed. Fluoride usually ends up in the solid phase of the waste; chloride, in the liquor phase.

Liquid phases of FGD wastes contain dissolved a variety of substances ranging from traces of a variety of metals to substantial amounts of commonly occurring ions such as sodium, calcium, magnesium, chloride, and sulfate. As was the case with composition of waste solids, concentrations of soluble substances in waste liquors can vary by two orders of magnitude or more. The total dissolved solids (TDS) level can vary from about 2,500 mg/liter to as much as 100,000 mg/liter, depending upon the chloride/sulfur ratio in the coal, type of system, and the extent to which solids are dewatered (and washed), if at all. However, because of the insolubility of many of the trace metal hydroxides only a very small fraction of each trace metal present in the waste is found dissolved in the waste liquor.

### (b) Physical Properties

For the most part, wastes are fine grained, with particle size distributions falling in the range of 5-50 microns, a range corresponding to silty to sandy soil. However, particles both smaller (< 1 micron) and larger (at least 200 microns) have been observed. Figure 5 shows particle size distribution curves for wastes sampled from a number of different operating FGD systems.

Viscosity of FGD wastes and the extent to which they can be dewatered depends upon the size and shape of the crystals and the quantity of fly ash present. The highest viscosities have been observed for agglomerated sulfite-rich crystals. These become difficult to pump at greater than 40% solids. They can be typically thickened to 20-40% solids and filtered to 40-75% solids. The lowest viscosities have been observed for wastes containing a high fraction of gypsum and/or fly ash. These wastes can be pumped in concentrations as high as 70% solids or more. Sulfate-rich wastes can usually be thickened to 30-60% solids and filtered to 60-90% solids.

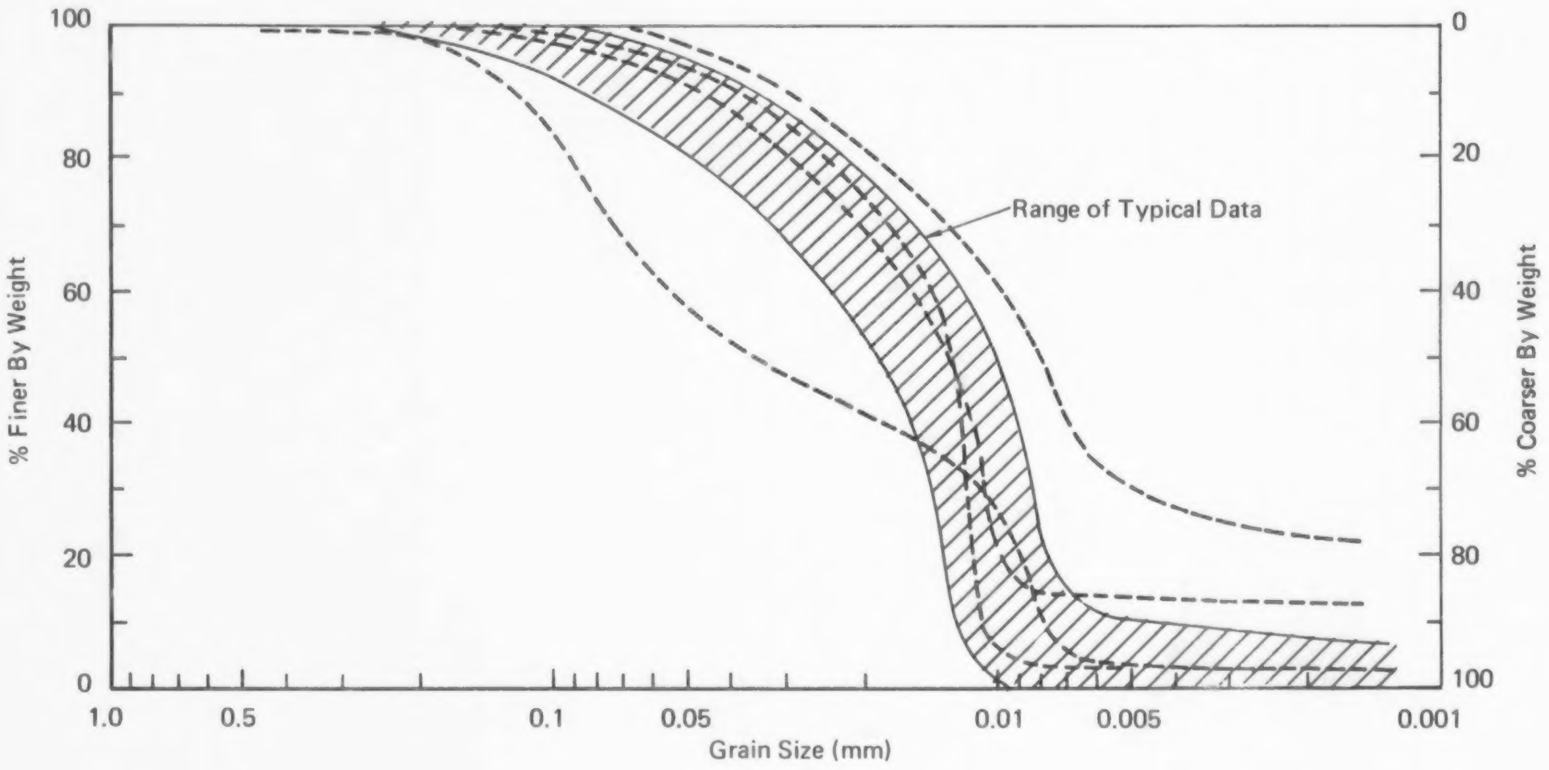


FIGURE 5 PARTICLE SIZE DISTRIBUTION OF FGD WASTES

If the solids content of FGD wastes is increased sufficiently by filtration, centrifugation, or other means as addition of fly ash, the waste can be compacted to a material which can be quite firm and which, if confined, can support considerable weight. However, the unconfined compressive strengths of such materials frequently range from nil to 20 psi.

### (c) Effects of Treatment

Treatment of FGD wastes by the addition of lime and fly ash (or similar source of silicate) can produce a relatively hard material when compacted. Such materials generally exhibit unconfined compressive strengths in the range of 100-400 psi (or higher). Treatment also tends to reduce permeability. Reported values of permeability coefficients for treated materials range from $10^{-5}$ to $10^{-7}$ cm/second, as compared with $10^{-4}$ to $10^{-5}$ cm/second for untreated compacted materials.

Preliminary data on leachate potential obtained from accelerated laboratory leach tests and field testing in ponds indicated that treatment, in addition to increasing strength and reducing permeability, may reduce the concentration of dissolved solids and the predominant soluble ions which constitute TDS in leachates. In addition, the improved handling properties of treated wastes in many cases should permit better control of waste placement and allow better management of the disposal site.

## 4. Impact Issues of FGD Waste Disposal in Coal Mines

There are four major impact issues to be assessed prior to any disposal of FGD waste in coal mines. These same basic issues are also most significant for other categories of mines, although the discussion in this paper is limited to coal, namely:

- groundwater contamination,
- surface water contamination,
- waste stability/consolidation, and
- fugitive air emission.

### (a) Groundwater Contamination

Groundwater contamination due to mine disposal of FGD waste varies with the type of mining technique employed, the climate where the mining occurs, and the geologic conditions of each mine. In surface coal mines, the degree of leachate production will be a function of whether the groundwater table is above or below the waste layer after disposal. In very deep underground mines, where the confining strata is dense and relatively impermeable because of overlying static loading, groundwater movement is very slow and the degree of recharge to surface water and wells would be very limited. Disposal of FGD waste in an underground mine which lies well above the groundwater table and is separated from the groundwater table by a relatively impermeable and plastic rock should also have minimal impact.

Leachate production from a waste deposit is a direct function of the rate of groundwater flow through the deposit. The flow would be limited by the waste (in-place) permeability as well as the surrounding strata permeability, depending on which is lower.

Initially, such water will flush interstitial waste liquors from the deposit. However, it may take tens to hundreds of years for one waste pore volume of groundwater to pass through a given waste deposit. Leachate from waste would move in a plume or a slug through the fractures and solution cavities of underlying strata until it eventually discharged to a downgradient well or surface water. The significance of the leachate would then depend on both baseline groundwater and leachate concentration levels and the use of the downgradient aquifer as a water supply.

Leachate concentrations would not be greater than the initial liquor concentrations (see Table 2) and after the first flush would not exceed equilibrium concentrations. According to laboratory testing, most of the total dissolved solids in waste liquor are calcium, magnesium and sodium chlorides and sulfates, which are not attenuated or precipitated to any measurable degree. Only a small amount of the total dissolved solids is attributed to trace elements such as arsenic, boron, cadmium, chromium, copper, lead, mercury, and zinc. In the mine disposal cases, the FGD waste is not mixed with soil matrix to provide attenuation through cation exchange capacity, and iron present in mine drainage may not be in a form which encourages precipitation.

Selenium and chromium are expected to be especially troublesome solubles in the leachate because they dominantly appear in the anionic form in waste and are therefore not affected by cation exchange and cation oxide precipitation mechanisms. Arsenic and boron are expected to leach because they are not readily precipitated, absorption being their primary mechanism of attenuation. Aluminum, beryllium, cadmium, copper, cobalt, iron, lead, manganese, mercury, molybdenum, nickel, and zinc are expected to be partially attenuated by precipitation mechanisms under the neutral to alkaline pH conditions. Where limestone is present, carbonate salts may form with cadmium, copper, iron, lead, and zinc. With acidic background groundwater, potential for precipitation of metals is limited.

It is recognized that total dissolved solids and trace elements in leachate may be of prime concern. The leaching of sulfite or total oxidizable sulfur (TOS) from wastes is also of concern. Since it is readily oxidized to sulfate, TOS represents an immediate oxygen demand to groundwaters and receiving waters. TOS may also be potentially toxic to aquatic life.

Sulfite can be present in the waste in two forms: as soluble sulfite (or bisulfite) in the liquor occluded with the waste; and in the waste solids as calcium (and magnesium) sulfite. The amount of sulfite in the waste will depend upon a number of factors which affect the degree of oxidation of absorbed $SO_2$. The principal factors are the type of FGD process in which the waste is produced, the operating conditions of both the FGD process

## TABLE 2

## LEVELS OF CHEMICAL SPECIES IN FGD WASTE LIQUORS AND ELUTRIATES

| | Eastern Coals | | | Western Coals | | |
|---|---|---|---|---|---|---|
| Species | Range in Liquor (ppm) | Median (ppm) | Total No. of Observations | Range in Liquor (ppm) | Median (ppm) | Total No. of Observations |
| Antimony | 0.46-1.6 | 1.2 | 4 | 0.09-0.22 | 0.16 | 2 |
| Arsenic | < 0.004-1.8 | 0.020 | 15 | < 0.004-0.2 | 0.009 | 7 |
| Beryllium | < 0.0005-0.05 | 0.014 | 16 | 0.0006-0.14 | 0.013 | 7 |
| Boron | 41 | 41 | 1 | 8.0 | 8.0 | 1 |
| Cadmium | 0.004-0.1 | 0.023 | 11 | 0.011-0.044 | 0.032 | 7 |
| Calcium | 470-2,600 | 700 | 15 | 240-(∼45,000)[b] | 720 | 6 |
| Chromium | 0.001-0.5 | 0.020 | 15 | 0.024-0.4 | 0.08 | 7 |
| Cobalt | < 0.002-0.1 | 0.35 | 3 | 0.1-0.17 | 0.14 | 2 |
| Copper | 0.002-0.4 | 0.015 | 15 | 0.002-0.6 | 0.20 | 7 |
| Iron | 0.02-0.1 | 0.026 | 5 | 0.42-8.1 | 4.3 | 2 |
| Lead | 0.002-0.55 | 0.12 | 15 | 0.0014-0.37 | 0.016 | 7 |
| Manganese | < 0.01-9.0 | 0.17 | 8 | 0.007-2.5 | 0.74 | 6 |
| Mercury | 0.0009-0.07 | 0.001 | 10 | < 0.01-0.07 | < 0.01 | 7 |
| Molybdenum | 5.3 | 5.3 | 1 | 0.91 | 0.91 | 1 |
| Nickel | 0.03-0.91 | 0.13 | 11 | 0.005-1.5 | 0.09 | 6 |
| Selenium | < 0.005-2.7 | 0.11 | 14 | < 0.001-2.2 | 0.14 | 7 |
| Sodium | 36-20,000[a] | 118 | 6 | 1,650-(∼9,000)[a] | -- | 2 |
| Zinc | 0.01-27 | 0.046 | 15 | 0.028-0.88 | 0.18 | 7 |
| Chloride | 470-5,000 | 2,300 | 9 | 1,700-43,000[b] | -- | 2 |
| Fluoride | 1.4-70 | 3.2 | 9 | 0.7-3.0 | 1.5 | 3 |
| Sulfate | 720-30,000[a] | 2,100 | 13 | 2,100-18,500[a] | 3,700 | 7 |
| TDS | 2,500-70,000[a] | 7,000 | -- | 5,000-95,000[b] | 12,000 | 3 |
| pH | 7.1-12.8 | -- | | 2.8-10.2 | -- | |

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[a] Levels of soluble sodium salts in dual alkali waste (filter cake) depend strongly on the degree of cake wash. The highest levels shown reflect single measurements on an unwashed dual alkali filter cake. (See text.)

[b] Levels of soluble chloride components in wastes are dependent upon the chloride-to-sulfur ratio in the coal. The highest levels shown are single measurements for a western limestone scrubbing system operating in a closed-loop using cooling tower blowdown for process makeup water.

and the boiler, and the characteristics of the coal fired. The manner in which the waste is processed (e.g., further dewatered, admixed with ash, etc.) and handled prior to and during disposal can also significantly affect sulfite levels due to sulfite oxidation by the air. Sulfite levels initially in the liquor phase of FGD waste can range from nil to hundreds of ppm. Similarly, the amount of sulfite in the waste solids can vary from nil to greater than 95% of the total calcium-sulfur salts present.

Since permeation of groundwater through the waste would normally be much slower than the dissolution rate(s) of the solids, the leachate would be expected to be saturated with respect to calcium sulfite. Saturation levels of sulfite would be dictated, then, by the solubility product of calcium sulfite and would depend principally upon the ionic strength and calcium concentration of the leachate.

Laboratory tests conducted at Arthur D. Little, Inc., using simulated groundwater indicate equilibrium sulfite concentrations on the order of 30 to 70 ppm for sulfite-rich wastes. Within this range sulfite concentrations increase with decreasing groundwater hardness ($Ca^{++}$ = 6 to 234 ppm), and increasing ionic strength ($\mu$ = 0.01 to 0.033 M). These results are consistent with prior data on leaching of sulfite-rich wastes using distilled water.

There are a number of factors, though, other than ionic strength and calcium concentration which can importantly affect the actual levels of sulfite achieved and the quantity of waste dissolved in any given disposal situation. These include:

- The relative amounts of sulfite and sulfate solids in the waste and the crystalline morphology of the waste--the less sulfite present, the lower the equilibrium sulfite concentration.

- The oxygen content of the groundwater--oxidation of sulfite will generally not appreciably change the final TOS concentration, but it may increase the rate of sulfite-rich waste dissolution.

- The groundwater acidity and the waste alkalinity--relatively high groundwater acidity can increase sulfite dissolution if not neutralized by the waste; however, if neutralized by the waste it can actually decrease soluble sulfite levels due to increased calcium concentrations.

- The presence of microorganisms which can catalyze chemical reactions and affect the local balance of sulfur species (oxidation/reduction).

Factors to consider in mitigating the degree of groundwater contamination are the site selection, oxidation achieved within the scrubbing process, waste dewatering, waste treatment, in-field waste compaction, and altered waste placement procedures (e.g., placing waste in a surface mine's spoil bank rather than at the base of the worked out pit).

In certain instances, FGD waste disposal may improve groundwater quality. For mines experiencing acid drainage, FGD waste disposal may limit formation of acidity by sealing the reactive pyrite from air exposure and resulting oxidation and disposal of alkaline FGD wastes may buffer the existing acid drainage. Limestone waste (with significant concentrations of unreacted calcium carbonate) is probably best for such neutralization.

### (b) Surface Water Contamination

Surface water contamination can originate along 3 pathways: contaminated groundwater recharge, contaminated surface runoff, and mine drainage effluent discharge. The extent to which any source is significant depends on the relative flow of the contaminated source to the assimilating flow of the receiving surface stream within the mixing zone. For example, if sulfite concentrations in leachate are about 20ppm, the depletion of oxygen in a stream having dissolved oxygen level of 7ppm would not be significant if the relative flows of surface water to leachate were five to one. The chemical constituent contribution of FGD waste to any of the three pathways would be comparable to the levels found in leachate. Therefore, the contributions would not exceed the initial liquor concentrations during first flush (see Table 2) and equilibrium concentration thereafter.

### (c) Physical Stability/Consolidation

Physical stability/consolidation of FGD waste in a mine depends largely on physical engineering properties of the waste as well as the engineering design for disposal. Untreated FGD wastes are fine grained and generally behave like inorganic silts or fine sands. The FGD wastes usually have a high moisture content (subject to partial dewatering by filtration as centrifugation) and are uncohesive and nonplastic. As a result, they are subject to settlement and to liquefaction after placement.

Soil mechanics testing indicates that admixture of FGD waste with soil or fly ash to increase solids content has a positive effect on shear strength characteristics (increasing cohesion and decreasing the angle of internal friction) and on consolidation (decreasing compression indices). Similarly, compaction at optimum moisture increases sheer strength and decreases consolidation.

In-field engineering precautions may also be used to ensure the stability of the waste disposal area. In surface mines, some overburden may be placed as an embankment in the worked-out pit to contain the dumped FGD waste.

Because of the sulfate, sulfite and chloride levels typical of FGC waste, it is expected to corrode concrete and steel. Therefore, bulkhead construction would probably require utilization of corrosion-resistant Type V Portland Cement, low water-to-cement weight ratios and epoxy-coated steel.

### (d) Fugitive Air Emissions

Fugitive air emissions which result from essentially uncontrolled nonpoint sources (versus controlled point sources such as stacks or vents) are the most difficult of all emissions to monitor. No definitive research has been done to develop fugitive factors for various types of FGD waste as influenced by moisture content, age, manner of storage and meteorological conditions (wind, temperature, etc.). In general, under normal wind velocities, inorganic particles having diameters larger than 74 microns (No. 200 mesh) tend to settle out of the air in less than 100 feet, and particles with diameters less than 30 microns have drift potentials in excess of 1000. Based on available particle size distribution data, wastes produced by FGD systems are generally fine grained (less than 74 microns). Pure sulfate crystals in wastes tend to be fine sand size, while sulfite and mixed sulfite/sulfate crystals tend to be silt size. Therefore, depending on the oxidation achieved in the FGD system, the portion of particle sizes below 74 microns can range from approximately 60% to 95%.

Particles less than 2 microns in size have been referenced as being a potential health hazard because they can reach the lungs and cause an irritation possibly leading to a form of pneumoconiosis. The portion of waste of particle size less than 2 microns is usually on the order of 5% or less. As a result, it is expected that of the dry waste which could be windblown as individual particles, only a minor portion would be susceptible to human inhalation and retention.

Based on field and laboratory observation, if the surface of FGD waste is exposed to a drying atmosphere for more than a week it would represent a particulate pollutant source. Activity associated with transport and handling accelerates drying and increases the susceptibility to becoming airborne. During stockpiling of dewatered FGD waste, emission may be limited by continuously spraying the piles with a fine water mist. Operations may be scheduled so that the waste surface is continuously renewed, by either adding moist fresh waste or removing dry exposed waste. During transport of waste by truck or rail, covering may be required. Also, chemical treatment of FGD waste may be used to aggregate particles. Treatment techniques which result in a soil-like product may have only a slight effect on the particle size distribution and would likely have little beneficial impact on fugitive emissions. However, fixation techniques which create FGD waste products resembling a soil-cement or low-strength concrete offer potential as mitigative measures.

A potential gaseous fugitive emission would be sulfur dioxide. When FGD waste is exposed in a mine environment containing acid mine drainage, it is possible that the calcium sulfite portion of the waste will react with the sulfuric acid in the drainage and release sulfur dioxide gas. This reaction would be expected to occur only in the initial period following disposal, because the buffering capacity of the waste would eventually raise the pH of the mine drainage.

Over the long term, microbial activity could cause $SO_2$ evolution. In a closed aqueous environment with faculative anaerobes oxidizing organics (e.g., coal), dissolved oxygen would be reduced first. In sequence, nitrate, manganese oxide, ferrous hydroxide, sulfate and carbon dioxide would then be reduced. With dissolved oxygen in groundwater being limited (probably less than 3ppm), and the other oxygen sources listed also present in minor amounts, it is likely that sulfate would be microbially utilized as an oxygen source. Long-term formation of calcium sulfite and resulting evolution of $SO_2$ may result.

Mines may suddenly belch gas when there is a drop in barometric pressure. Therefore, over the long term, sulfur dioxide in equilibrium within the waste deposit could suddenly be out-gassed as the weather changed and the barometric pressure dropped.

$SO_2$ evolution could represent a potential health problem for mine workers. If $SO_2$ adsorbs onto dust in the mine, it has an increased likelihood of being ingested and causing damage within a worker's lungs. OSHA recommends an eight-hour average Threshold Limit Value for $SO_2$ of 5 ppm. In a mine, dilution is a function of the mine dimensions and the ventilation throughput. The amount of $SO_2$ evolution is a function of the final pH of the mine drainage/FGD waste solution and the amount of waste surface area exposure relative to the amount of mine drainage. For a specific FGD waste disposal proposal, the expected release of $SO_2$ from a specific waste could be estimated and the ventilation throughput requirements could conceivably be determined. Also, the potential for long term $SO_2$ evolution can be minimized by decreasing the available waste surface area through chemical treatment.

Based on the potential adverse health effects to miners within a closed underground mine environment from $SO_2$ evolution, FGD waste should not be placed in mines where the drainage has a pH less than 4.

### 5. Regulation of Mine Disposal

Regulation applicable to the four major impact issues discussed above is accomplished under nine major federal laws. See Table 3 for a list of the impact issues with the corresponding legislation and administrative body. While some environmental degradation is expected from disposal of FGD waste, enforcement of these laws should adequately limit their significance in terms of public health and safety. For example, although some groundwater degradation attributed to leachate concentrations of total dissolved solids, trace metals and TOS would occur, enforcement of the Resource Conservation and Recovery Act and the Safe Drinking Water Act would limit degradation within those ranges considered acceptable for the aquifer's intended uses.

The main thrust of each law as it applies to disposal of FGD waste in coal mines is summarized in the following paragraphs. The laws governing protection of miner/worker health and safety and transportation of the wastes rely heavily on federal enforcement. The other laws discussed below rely on state enforcement programs modeled after guidance and criteria developed by federal agencies.

## TABLE 3

## REGULATION OF FGD WASTE DISPOSAL IN COAL MINES

| Impact Issue | Legislation | Administrator |
|---|---|---|
| Ground Wastes Contamination | • Resource Conservation and Recovery Act of 1976 | • Environmental Protection Agency |
| | • Safe Drinking Water Act of 1974 | • Environmental Protection Agency |
| Surface Water Contamination | • Federal Water Pollution Control Act Amendments of 1972 | • Environmental Protection Agency |
| Waste Stability/ Consolidation | • Surface Mining Control and Reclamation Act of 1977 | • Office of Surface Mining Reclamation and Enforcement |
| | • Dam Safety Act of 1972 | • Army Corps of Engineers |
| | • Federal Coal Mine Health and Safety Act of 1969 | • Mining Enforcement Safety Administration |
| | • Occupational Safety and Health Act of 1970 | • Occupational Safety and Health Administration |
| Fugitive Air Emissions | • Clean Air Act of 1974 | • Environmental Protection Agency |
| | • Federal Coal Mine Health and Safety Act of 1969 | • Environmental Protection Agency |
| | • Occupational Safety and Health Act of 1970 | • Environmental Protection Agency |

The Resource Conservation and Recovery Act is the major legislation regulating environmental protection (e.g. groundwater protection) from mine disposal of FGD waste. Section 4004(a) of the Act requires development of environmental criteria to classify disposal areas as either open dumps or sanitary landfills. The criteria is expected to address land disposal broadly--including impoundments, land spreading, and surface mine disposal. Following the promulgation of criteria, state plans will be developed so that existing open dumps will be closed or upgraded and future land disposal will meet sanitary landfill criteria. The criteria are expected to prohibit any groundwater contamination which would require additional groundwater treatment for intended uses. To achieve the criteria, it is likely that either: sites would be lined or have adequate impermeability and soil attenuative capacity to protect groundwater quality (unlined sites must also have a contingency plan to amend contamination when/if it occurs), or the waste would be chemically treated (e.g., admixed with fly ash and lime).

Under the Safe Drinking Water Act, states are required to adopt programs prohibiting underground injection of wastes without a permit. Regulations for the state underground injection control programs were promulgated by the Federal EPA and apply to all deliberate subsurface emplacement of wastes by wells. The principal regulatory objective is protection of groundwater from endangerment of viable drinking water sources. The regulations would apply to underground mine disposal of FGD wastes through boreholes, and would be likely to require either: disposal of chemically treated wastes, or disposal within an underground region that does not recharge a viable drinking water source.

FGD waste disposal would affect regulation of effluent discharges under the Federal Water Pollution Control Act Amendments. Current Effluent Limitation Guidelines are based on the principal chemical constituents typically found in mine drainage. Introduction of a waste material could alter the designation of significant constituents which should be limited, as well as the final effluent concentrations which are achievable by available technology, resulting in a need to modify the Effluent Limitation Guidelines.

Under the Surface Mining Control and Reclamation Act, placement of any waste within a surface mine is prohibited if it would pose an environmental or health hazard or cause physical instability of the mine area. Actual mine disposal regulation for purposes of groundwater protection would probably occur under the Resource Conservation and Recovery Act and disposal would probably have to meet sanitary landfill criteria. However, the physical stability of FGD waste storage piles or mine disposal areas would be regulated under this Act. The physical stability of wastes impounded by a dam during storage could be regulated under the Dam Safety Act. Under this Act, an initial inspection and inventory of existing dams was accomplished along with recommendations of dam specifications and inspection procedures to be included in further laws and regulations. Eventually, states will establish their own programs consistent with federally provided model legislation and guidelines.

Standards promulgated under the Federal Coal Mine Health and Safety Act are designed to protect miners from accidents and disease. For example, the standards apply to air contamination from fugitive air emission of particulates or sulfur dioxide, noise, waste stability, and safeguards for mechanical and electrical equipment. Similarly, standards promulgated under the Occupational Safety and Health Act would focus on protecting workers in all aspects of FGD waste disposal outside of the mine fenceline.

The Clean Air Act would be the primary vehicle for regulating regional distribution of fugitive air emissions which may result from uncontrolled nonpoint sources involved with the handling and storage of FGD waste. Regulation would be accomplished under provisions of the Act requiring that no emitting source interfere with the achievement and maintenance of National Ambient Air Quality Standards (e.g., standards for sulfur oxides and particulates). In some cases, chemical treatment of waste or dust suppression methods may be required.

## 6. Summary

Based upon the potential impacts of mine disposal of FGD waste and the anticipated regulatory requirements, there are four principal operational parameters that can be used to minimize the significance of impacts to the environment and public health:

- scrubber system operation (waste characteristics);
- site selection (site geology);
- waste treatment; and
- placement procedures.

The type of scrubber system and the manner in which it is operated is generally dependent upon the type of coal burned and the $SO_2$ emissions regulations. Together, these dictate the chemical and physical characteristics of the wastes--the levels of soluble solids, trace metals and sulfite; the buffering capacity (pH); and the particle size distribution and crystalline morphology. The sulfite/sulfate ratio in the wastes which affects the potential for $SO_2$ evolution and TOS release is determined by the degree of oxidation in the scrubber system. The solubles content of the wastes depends primarily on the type of system (lime, lime with Mg addition, double alkali, etc.), the composition of the coal (ash) and the degree of oxidation. The level of trace metals varies with the ash composition and the quantity of ash (admixed or simultaneously removed) in the wastes. The quantity of ash along with the particle size distribution and crystalline morphology of the calcium sulfur salts, and the degree of waste dewatering determine the potential for fugitive emissions and liquefaction.

Site selection can affect not only the amount of leachate produced from FGD waste disposal, but also the degree of corresponding groundwater contamination. In general, disposal sites should not have a direct hydraulic connection with a useable groundwater supply; nor should there be a direct connection with small streams having limited assimilative capacity relative to the flow rate of contaminated groundwater. Site selection is also important in terms of background groundwater quality, as it can affect the dissolution rate of the chemical constituents in the wastes.

Both chemical treatment and compaction serve to increase the dry density of the waste, decrease the waste permeability and decrease the exposed waste surface area. As a result leaching, liquefaction, consolidation, and fugitive air emission impact potential can be lessened. The improved handling properties of treated wastes should in many cases permit better control of waste placement and better management of the disposal operation.

Placement procedures can affect the impacts by further isolating the FGD waste from groundwater and surface area (e.g., placement in a surface mine spoil bank) or containing the waste (e.g., bulkheads). Placement in combination with proper site selection and management probably ranks as the most important single method of controlling adverse impacts.

In general, the cost of mine disposal is expected to be comparable to that of other land disposal options, and in many cases may be considerably lower. In an active mine there are no direct land costs (except as included as part of a fee), and, since the disposal can be carried out as part of reclamation activities, in most cases there should be minimal earthmoving or site construction over that required for the normal reclamation. As in other disposal operations, costs can be quite sensitive to transport mode and distance and the degree of treatment and control required.

# POTENTIAL MARKETS FOR SULFUR DIOXIDE ABATEMENT PRODUCTS

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## ABSTRACT

Air quality regulations require control of sulfur oxides emissions from power boilers. Recovery of sulfur in useful form would avoid waste disposal and conserve natural reserves. Marketability of byproducts is an uncertainty. Two EPA-sponsored studies were conducted by TVA to evaluate market potential for gypsum byproducts, sulfur, and sulfuric acid. A cost model was developed to estimate the least cost compliance method from three alternatives: (1) selecting a clean fuel strategy, (2) selecting a limestone throwaway scrubbing technology, or (3) selecting a sulfuric acid-, gypsum-, or sulfur-producing scrubbing technology. For plants where production of byproducts was the economic choice, a market simulation model was used to evaluate distribution of byproducts in competition with existing markets. Significant amounts of sulfuric acid could be produced from sulfur oxides in power plant flue gas and sold in competitive markets. Production and sale of byproduct gypsum have potential for control of a minor portion of the required reduction in sulfur oxides emissions.

# POTENTIAL MARKETS FOR SULFUR DIOXIDE ABATEMENT PRODUCTS

Air quality regulations require fossil fuel-fired power plants to meet emission limitations on sulfur oxides formed when sulfur in the fuel is burned. The current alternatives are use of low-sulfur fuel that meets the emission regulation or use of flue gas desulfurization (FGD) technology to remove sulfur oxides after the fuel is burned. Other technology to convert high-sulfur fuels to clean gas or liquids is being developed but is not fully developed.

The electric utility industry would generally prefer use of complying fuel. However, coal supplies that meet the emission regulations are in short supply in the eastern part of the country where a major portion of the power is produced. Some of the coal in the Western States is sufficiently low in sulfur to meet the present New Source Performance Standards (NSPS), but limitations on mining and transportation facilities reduce the potential of this fuel supply for use in the industrial East. Moreover, proposed changes to the regulations could prevent use of coal from regions outside the area of use.

FGD technology is still in the development stage, but several power companies have installed FGD systems to comply with the regulations while burning high-sulfur fuel. Most of the processes are based on scrubbing with lime or limestone and produce sludge that must be discarded in storage ponds. This practice commits large land areas to nonproductive use. Technology for recovery of sulfur in useful form is also under development. These processes will provide an alternative to producing waste solids and will allow conservation of natural sulfur reserves. An effective method for evaluating market potential of recovered products and for identifying the most likely mix of compliance strategies is needed to provide guidance to the utility industry in selecting from alternative systems.

In order to provide perspective on the potential use of recovery technology, EPA contracted with TVA to carry out a series of studies to develop a method for comparison of FGD systems to evaluate market potential for abatement products, to characterize and identify power plants that are the most likely candidates for producing useful products, and to characterize and identify the most likely demand points for the byproducts.

The following paper presents in two separate sections the results of a sulfuric acid market study and a gypsum market study.

# POTENTIAL ABATEMENT PRODUCTION AND MARKETING OF BYPRODUCT SULFURIC ACID IN THE UNITED STATES

## INTRODUCTION

Emission control regulations for the electric power industry require utilities to either burn fuel with a low enough sulfur (S) content to meet the standard or to remove a portion of the S before, during, or after combustion. Coal is the predominant fuel for power boilers and its use will increase. Utilities prefer use of complying coal compared to other alternatives for control. However, low-S coal is not generally available near the areas of high electricity demand. Technology for removal of S from coal prior to or during combustion is being developed but will not make a substantial contribution to control in the near term. The primary alternative to use of low-S fuel is removing sulfur oxides ($SO_x$) from the flue gas produced when the coal is burned in the boiler. Use of flue gas desulfurization (FGD) technology currently accounts for only a minor portion of the control required, but its use is growing as a result of limited alternatives to meet compliance schedules. Most applications are based on lime and limestone scrubbing. These methods produce high volumes of waste solids for utilization or ultimate disposal. Technology for recovery of S in useful form is being developed and, when available, will provide an alternative to production of waste solids. Recovery of S from flue gas would conserve natural S reserves and reduce the requirement for energy used in mining S. One of the major uncertainties associated with this approach is the marketability of recovered S byproducts.

In this study sponsored by EPA, TVA has evaluated the potential markets for S and sulfuric acid ($H_2SO_4$) that could be economically produced by the power industry as an alternative to use of clean fuel or limestone scrubbing. A market simulation model was developed to evaluate distribution of byproducts from smelters as well as power plants in competition with the existing markets based on an assumed S price of $60/long ton. This value of S is representative of projected costs of production. Recovery of S from gas and oil was not included in the study although delivered price of S reflects this competition.

## CONCLUSIONS

A greater portion of future supply of S will have to come from other than natural sources. Beyond the year 2000, the demand will exceed the supply of natural S.[1] Recovery of S byproducts from coal combustion could make a substantial contribution to the additional supply.

The entire U.S. electric utility industry was characterized from Federal Power Commission (FPC) data with respect to plant age, fuel type, capacity, load factors, and $SO_x$ emission rates for the operating year 1978. Out of a total of 3382 boilers located at 800 power stations, 833 boilers at 187 stations were projected to be out of compliance with current applicable emission regulations. The total $SO_x$ emissions from these 187 plants is equivalent to 17.5 million tons of $H_2SO_4$; total $H_2SO_4$ consumption was estimated to be 32.2 million tons in 1978. Therefore the total market is about twice the potential byproduct production.

For the plants estimated to be out of compliance, limestone scrubbing is generally the least-cost scrubbing method when credit for byproduct sales is not included but when credit is applied, production of byproducts becomes competitive; of the alternatives considered in this study using currently applicable technology, production of $H_2SO_4$ was less expensive than production of S. An alternative to use of scrubbing was provided by comparing the cost of scrubbing with selected values of premium cost of complying fuel. The values were selected to determine the effect on potential volume of abatement products.

When the clean fuel premium was set at \$0.70/MBtu (M = one million), the mix of least-cost compliance methods was:

| | |
|---|---|
| Purchase complying fuel | 71 plants |
| Use limestone scrubbing | 87 plants |
| Produce byproduct acid | 29 plants |

The amount of acid produced and marketed totaled approximately 6 million tons; an additional 5 million tons could have been produced at a lower cost than the alternative compliance method selected but could not be sold in competition with acid produced from elemental S priced at \$60/ton. The simulation model was designed to allow the nonferrous smelter industry to compete with the utility industry for byproduct markets. The total byproduct acid supplied from both industries was 7.11 million tons or 22% of the total $H_2SO_4$ market; however, some of the plants that are good candidates for recovery may be implementing other compliance plans. The control of sulfur dioxide ($SO_2$) emissions in the utility industry through use of recovery technology could contribute 56% of the estimated total reduction needed for the industry to be in compliance. Further use of recovery technology will depend primarily on substantial increases in elemental S prices which are difficult to predict in the near term. Reduction in the cost of control technology would also increase the potential for increased production of byproducts, but the costs are not likely to improve significantly. Reduction in transportation costs is a more realistic possibility for improving economics of marketing byproduct acid. Higher levels of clean fuel premium would not affect the results since the supply at the maximum value studied exceeded the demand.

The development of data bases and programs for use of the model to predict byproduct market potential resulted in capability to perform other highly relevant calculations.

The scrubber cost generator may be used to estimate the investment and operating costs of alternative scrubbing systems for all existing and planned power plants. In this study, costs were estimated for limestone, magnesium oxide (MgO), and Wellman-Lord/Allied scrubbing systems for all plants projected to be out of compliance in 1978. For use in the study, relativity of costs was the primary interest. However, the input cost data could be refined to reflect special design considerations for specific plants to improve the accuracy of estimates.

The procedure for evaluating compliance status based on applicable standards and FPC projection of fuel characteristics may be used to estimate the effect of changing emission standards on the cost of compliance. This study was based on the State Implementation Plans (SIP) regulations that were in effect as of June 1976.

The transportation model that was developed to distribute byproduct acid from supply points to areas of use is a sophisticated program that has potential for extensive use. The model calculates actual, rate-base mileage between any two points on the established railway network. For this study, tariffs were incorporated for $H_2SO_4$ movements. Available tariffs for any other commodity could be incorporated to calculate actual transportation costs between any two points.

An important finding was that while long-run competitive equilibrium solutions predict what may happen in competitive markets they do not identify net social gain.

The savings to both industries at the \$0.70/MBtu clean fuel premium run resulting from absorption of abatement byproduct acid in the existing market amounted to \$122,877,000 or \$16.20/ton of acid utilized.

## METHODOLOGY

The objective of the overall marketing model is to simulate long-run competitive equilibrium market conditions for S and $H_2SO_4$ in the U.S. as might be impacted by production of abatement acid or S. To simulate these conditions, the cost to both the $H_2SO_4$ and the power plant industries is minimized subject to the condition that acid demand is met either from traditional S sources or from substitution of abatement $H_2SO_4$.

Analysis of the model addresses three choices for the steam plants that are not meeting the current SIP standards. These include (1) selecting a clean fuel strategy, (2) selecting a limestone-throwaway scrubbing technology, or (3) selecting an $H_2SO_4$ (MgO)- or S- (Wellman-Lord/Allied) producing scrubbing technology. In terms of the latter choice, study results indicate that abatement S cannot compete with abatement $H_2SO_4$ production at any location considered in the market simulation model; possibly new technology will reduce the costs. EPA is currently sponsoring work with Empire State Electric Energy Research Corporation (ESEERCO) and Niagara Mohawk to develop the Atomics International process for producing S from $SO_2$ in stack gas. This technology and other work involving use of solid reductants could lead to lower costs for production of S as an alternative to producing $H_2SO_4$. The incentive for production of S is high because it is a more convenient material to handle, requires less storage volume, and could be incorporated more easily into the existing market. Moreover, fluctuations in market demand could be met with less impact to both the producer and consumer.

The optimal solution predicts not only which acid producer would buy and which steam plant would sell $H_2SO_4$, but also which steam plant would sell to which acid plants. Any variations to this optimal solution would increase the total cost to both industries.

A flow diagram of the major system design requirements is outlined in Figure 1. The major data bases feed the market simulation model through cost generation models as follows:

1. Emission control requirements for $SO_x$ were determined for each power plant boiler, stack, or plant projected to operate in 1978 using the FPC data (Form 67), June 1976 SIP, and New Source Performance Standards (NSPS).

2. The scrubbing cost generator was developed to provide unit production costs for byproduct $H_2SO_4$, elemental S, and limestone-throwaway sludge including potential production quantities for each power plant boiler. It was designed as an economic screen to select the most efficient boiler combinations for meeting compliance on the basis of cents/MBtu heat input for each scrubbing system considered. The results of this screen provide the lowest cost method for compliance with given scrubbing technology. This information is fed to the market simulation model to identify both the relative efficiency as well as unique location advantages for all power plant boilers producing abatement acid in competition with byproduct smelter acid producers in the existing market. The marketing model then estimates long-run competitive equilibrium solutions based on realistic outputs of abatement byproducts by

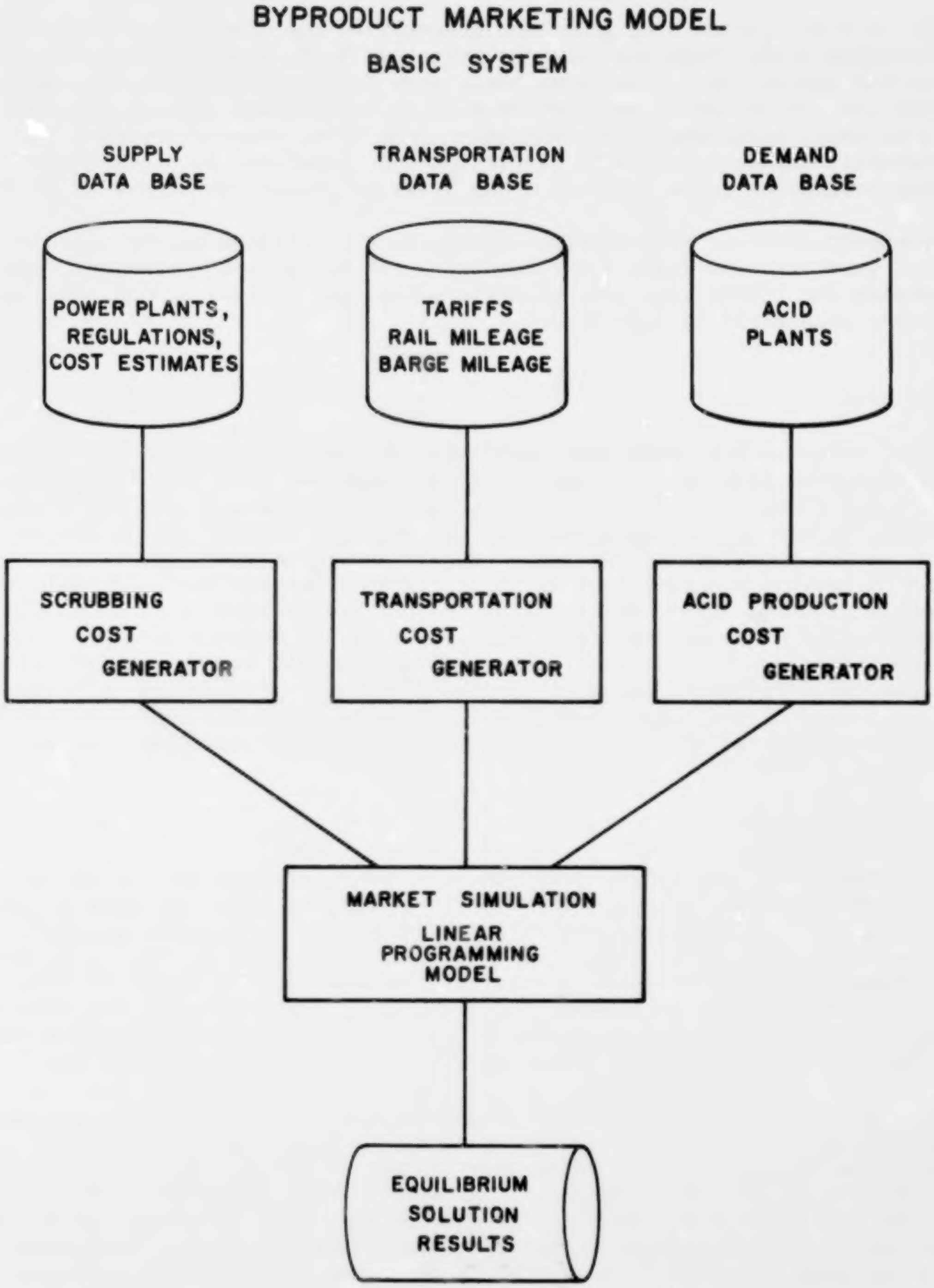
BYPRODUCT MARKETING MODEL
BASIC SYSTEM
SUPPLY DATA BASE
TRANSPORTATION DATA BASE
DEMAND DATA BASE
POWER PLANTS, REGULATIONS, COST ESTIMATES
TARIFFS RAIL MILEAGE BARGE MILEAGE
ACID PLANTS
SCRUBBING COST GENERATOR
TRANSPORTATION COST GENERATOR
ACID PRODUCTION COST GENERATOR
MARKET SIMULATION
LINEAR PROGRAMMING MODEL
EQUILIBRIUM SOLUTION RESULTS

Figure 1. Flow diagram for major system design requirements.

identifying major candidates for abatement byproduct production and consumption versus a limestone-throwaway strategy and/or the alternative of using a clean fuel.

3. The acid production cost generator encompasses the elemental S producers, the S-burning $H_2SO_4$ producers, and the byproduct $H_2SO_4$ producers associated with smelter operations. These data bases were developed from the TVA computerized data base on worldwide manufacturers of fertilizer and related products. This information supplemented by references from other sources provided the necessary inputs to the acid production cost generator to provide unit avoidable production costs for each $H_2SO_4$ plant projected to operate in 1978.

4. Transportation and distribution options were calculated by the transportation cost generator for $H_2SO_4$ and elemental S for all possible transfer combinations between the S producers, the electric utilities, smelter plants, and $H_2SO_4$ plants considered in this study.

## Compliance Test

The $SO_2$ emission and compliance model uses the projected annual fuel consumption and characteristics data to calculate the annual quantity of S that is emitted from each boiler and plant. For each plant, allowable emissions are calculated based on NSPS for new boilers or the applicable SIP for existing boilers taking into account heating value and S content of the fuel. Excess emissions expressed as tons of S which must be removed are estimated as the difference between the calculated actual and allowable values. The compliance test selects the applicable level of SIP as (1) an entire plant, (2) an individual boiler, or (3) an individual stack. In all cases where scrubbers could be used, they are designed for an $SO_2$ removal efficiency of 90%. However, the actual level of removel efficiency will depend on better definition of performance during sustained full-scale operation when coal is the fuel. The amount of gas scrubbed is based on increments of standard-size scrubbers.

## Scrubber Cost Generator

In all cases the $SO_2$ control strategy is selected on the basis of minimum cost for compliance. The data generated in the scrubbing cost model are used to calculate the scrubbing cost of a limestone-throwaway system versus a salable byproduct for each of the 833 boilers or combinations of boilers identified in this study that will be out of compliance with emission control regulations in 1978 (based on 1976 regulations). The cost is expressed as cents/MBtu for direct comparison with the clean fuel alternative. The alternative clean fuel level (ACFL) represents the premium that can be paid for complying fuel in lieu of using an FGD system.

The model also calculates cost differential between scrubbing with a limestone-throwaway system and scrubbing with MgO to produce $H_2SO_4$. This accommodates identifying the incremental cost difference of the two systems for all boilers or the combinations of boilers included in the model. This incremental cost becomes input to the marketing model which is designed to determine potential for production and marketing of abatement $H_2SO_4$ at various power plant locations. The comparative FGD costs for each power plant considered in the study can be used to generate a supply curve for the production of abatement $H_2SO_4$. The supply curve for abatement acid is presented graphically in Figure 2. This curve is estimated by ranking power plant boiler combinations from lowest to highest cost for producing abatement $H_2SO_4$ as a function of accumulated supply quantities.

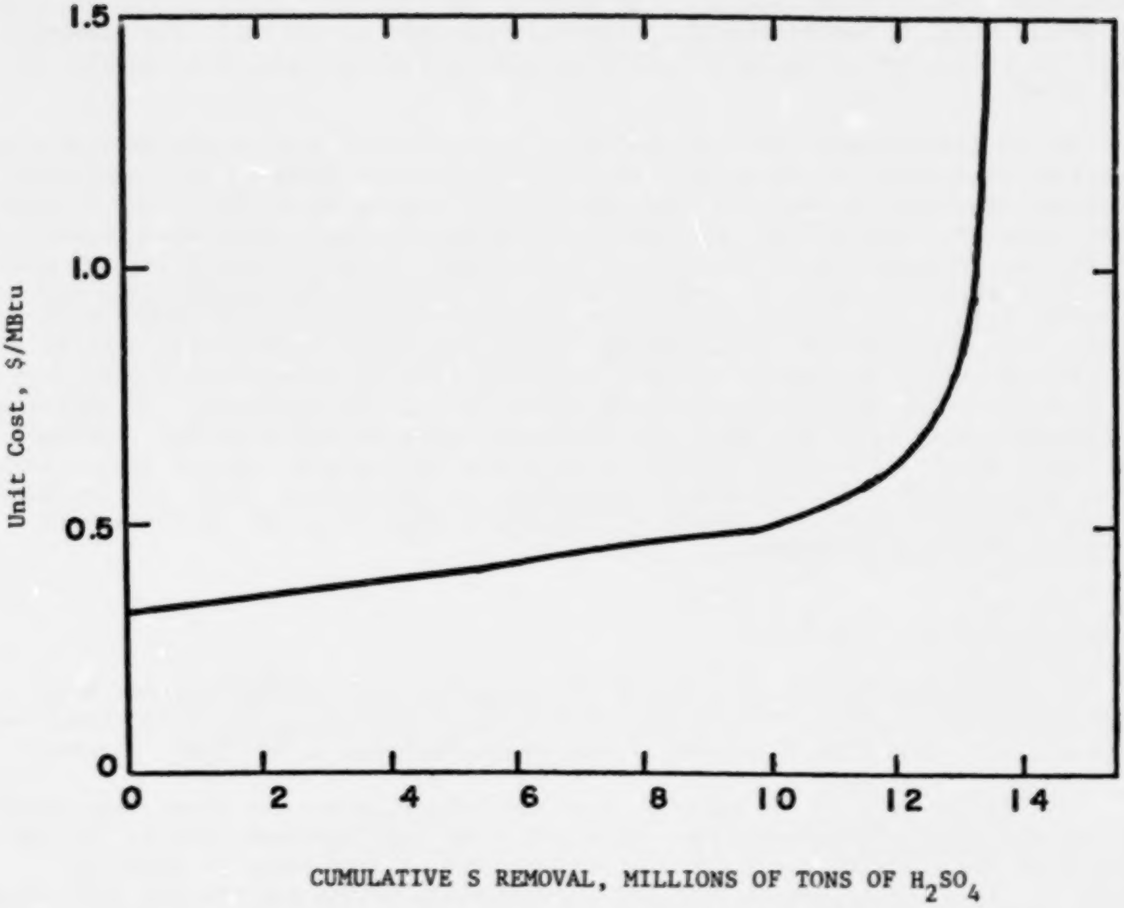

Figure 2. The supply cost curve for abatement acid.

## Acid Cost Generator

$H_2SO_4$ plants are widely scattered throughout the industrial sector of the U.S.; acid has been traditionally produced by S-burning plants in captive use near the point of consumption. In this study it was assumed that the $H_2SO_4$ market can be simulated as though all consumption occurs at the $H_2SO_4$ plants and that acid-producing firms will close these plants and buy abatement acid if it can be delivered at costs equal to or below their avoidable cost of production. Avoidable cost is an estimation of the production costs that could be avoided by closing an existing acid plant assuming abatement byproduct acid would be available in amounts equal to the plant production capacity (330 days/yr). To develop the required inputs to the model on the demand side, it was necessary to identify the acid plants that burn elemental S for the production of $H_2SO_4$ and calculate the avoidable costs of production at each plant.

The avoidable costs (theoretical) were calculated at each of the 90 acid plant locations considered in the study. Costs of manufacture based on data generated indicated that most of the acid production costs range from \$25.00 to \$45.00 depending on plant location, size, and age; the March 1976 price for $H_2SO_4$ (100% $H_2SO_4$ f.o.b.) was \$44.95/ton. A summation of capacity of acid plants versus avoidable cost of production is shown in Figure 3. The resulting plot defines the demand curve for abatement acid. The demand curve is estimated by ranking all acid plants from highest to lowest cost and accumulating demand quantities to show acid cost as a function of acid plant capacity. At a very high cost of alternative supply, only a few acid producers could justify buying rather than producing $H_2SO_4$. As supply cost of abatement acid declines, more acid producers would become potential customers. At low supply costs all but the largest, most modern acid plants located near S supplies could be shut down. The important implication for the present study is that small quantities of abatement acid could be marketed at high value but as the supply increases the value declines.

## Transportation Cost Generator

To assess representative competitive costs, a market system analysis must generate accurate S freight rates from the Frasch S sources to the acid plants and $H_2SO_4$ freight rates from all power plants and/or smelters to all $H_2SO_4$ plants.

The linkage used in the study between the S-$H_2SO_4$ and power plant data bases and the rate generation system is a standard point location code (SPLC). A flow diagram of the freight rate generation system used in this model is shown in Figure 4. This shows that an SPLC for a power plant origin and one for $H_2SO_4$ plant destination are input to the national rate base tariff. This tariff determines for rail rate purposes the basing points for the origin and destination. Output are two sets of codes used to define mileage and tariff rates between the byproduct shipping origin and destination points.

It is important to identify not only the mileage but also the tariff number. A slight error in mileage is not nearly as critical as knowing which tariff applies. Four tariffs were found in published $H_2SO_4$ rates. Rates for eight other tariffs were generated by TVA's Navigation and Regional Economics Branch from these using sound traffic legal arguments similar to the negotiation process that would ensue should large acid movements become a reality.

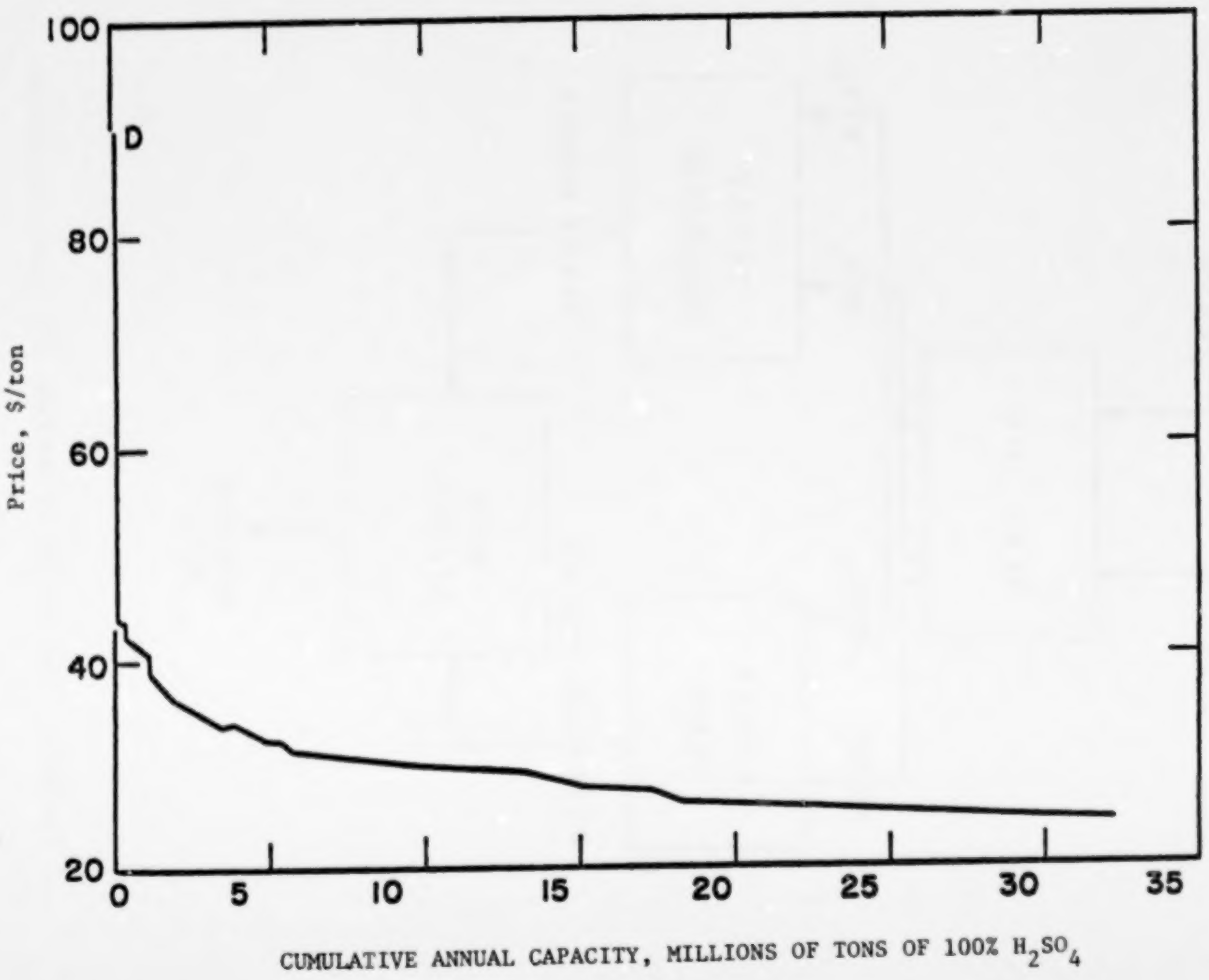

Figure 3. Abatement byproduct $H_2SO_4$ demand curve (eastern states).

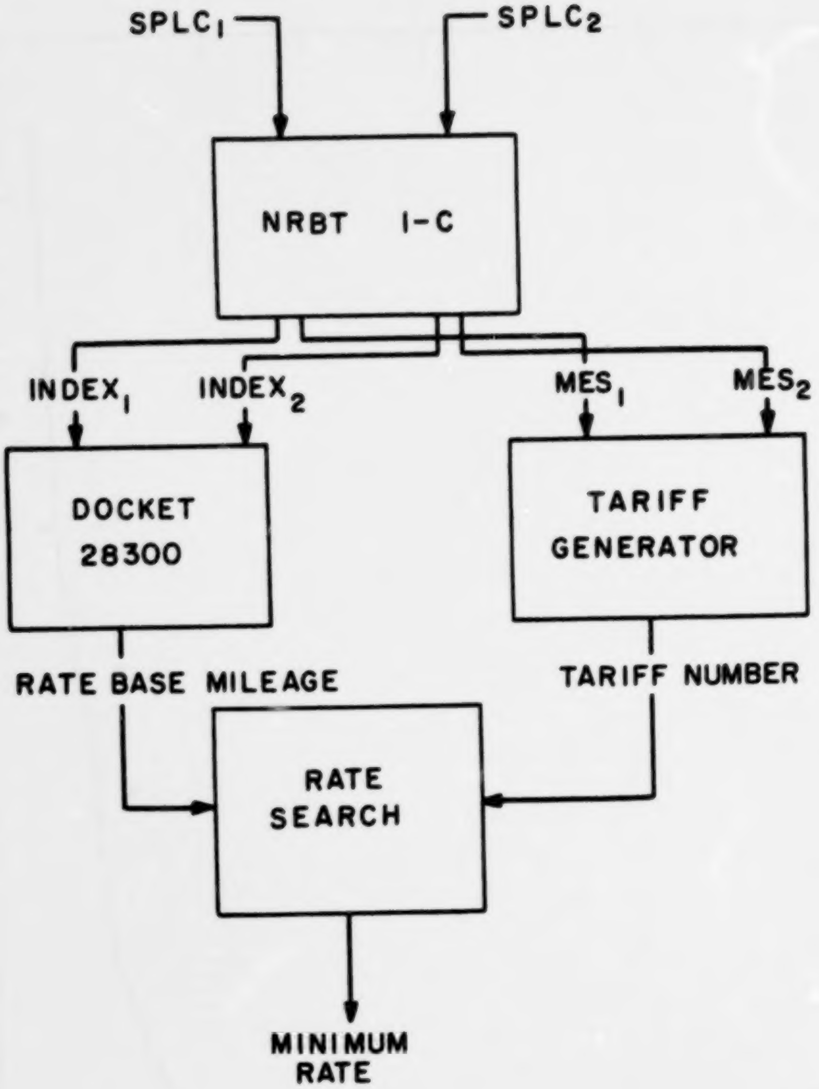

Figure 4. Flow diagram of freight rate generation model.

## RESULTS OF ANALYSES

### Sulfur and Sulfuric Acid Industry

The U.S. Bureau of Mines (BOM) reports the production of S in all forms in 1976 at 10.9 million long tons. Elemental S was produced by 69 companies at 182 plants in 32 states with 10 of the largest companies owning 57 plants and accounting for 75% of the output. The production was concentrated in Texas and Louisiana accounting for 68% of the total output. The Frasch S was produced in these two states at 12 mines, 5 of the largest mines accounting for 82% of the total Frasch output and 48% of the total production of S in all forms. Long-range prediction of S demand in millions of tons is shown below.

| | Forecast | | | |
|---|---|---|---|---|
| | 1976 | 1980 | 1985 | 1990 |
| Fertilizer | 6.4 | 7.5 | 9.3 | 11.0 |
| Industrial | 4.5 | 5.3 | 6.0 | 6.8 |
| Total | 10.9 | 12.8 | 15.3 | 17.8 |

Frasch S production is a mining operation. Wells are sunk into S-bearing strata, S is melted by hot water injected into the strata, and the molten S is pumped out. The molten S is pumped from the well to either heated tanks for storage as a liquid or to vats where it cools and solidifies. About 75% of the total mining costs of Frasch S is variable, such as the cost of natural gas to heat water, water treatment, labor, and operating supplies. The cost of hot water to melt the S is by far the most important cost and will differ drastically from mine to mine as water requirements and fuel cost differ. In an analysis prepared for this study the cost of natural gas was varied from \$0.20 to \$3.00/kft$^3$ (k = one thousand) with an intermediate value of \$1.00/kft$^3$. Water requirements or water rate varied from 1600 gal/ton of S produced to 9000 gal/ton of S. The results of this study indicated that the lowest capital investment and operating costs are associated with mines having low water rates and that cost increases markedly with increasing natural gas costs. For operation where the major variables are constant, i.e., water rate and natural gas cost, the usual economies of size prevail.

Most of the S consumed in the U.S. is used to produce $H_2SO_4$. Over two-thirds of the $H_2SO_4$ is used in the manufacture of fertilizers. A breakdown of the estimated consumption of S in all forms by end use is presented in Table 1.

### Characteristics of Power Plants

In 1973 utilities were requested by FPC to project fuel consumption and characteristics for 1978. The majority of utilities provided FPC with these projections. For the utilities which did not project this information, fuel consumption and characteristics reported for 1973 were used. Based on the updated projections, Table 2 shows the consumption rates and characteristics of fossil fuels projected to be utilized during 1978. For plants which use multiple fuels and did not project their 1978 consumption, a method for projecting distribution of fuel type developed.

A comparison of the total projected 1978 coal, fuel oil, and gas consumption with the historical 1973 fuel consumption by region is shown in Table 3. The

## Table 1. U.S. CONSUMPTION OF SULFUR IN ALL FORMS BY END USE

(Thousand long tons S equivalent)

| | 1974 | 1975 | 1976 |
|---|---|---|---|
| $H_2SO_4$ | | | |
| Fertilizer acid | | | |
| $H_3PO_4$ | 4,945 | 5,410 | 5,560 |
| Normal superphosphates | 405 | 290 | 230 |
| $(NH_4)_2SO_4$ and other | 685 | 670 | 610 |
| Total fertilizer acid | 6,035 | 6,370 | 6,400 |
| Industrial acid | 3,715 | 3,080 | 3,285 |
| Total $H_2SO_4$ | 9,750 | 9,450 | 9,685 |
| Non-acid | 1,250 | 1,200 | 1,215 |
| Total in all forms | 11,000 | 10,650 | 10,900 |

## Table 2. PROJECTED 1978 FOSSIL FUEL CONSUMPTION RATES AND CHARACTERISTICS

| | All plants | Plants out of compliance |
|---|---|---|
| Coal | | |
| Total consumption | | |
| ktons[a] | 475,600 | 226,800 |
| GBtu[b] | 10,408,300 | 5,125,000 |
| Heating value, Btu/lb | 10,943 | 11,300 |
| S content, % by wt | 2.12 | 2.81 |
| Equivalent $SO_2$ content, lb $SO_2$/MBtu[c] | 3.87 | 4.97 |
| Oil | | |
| Total consumption | | |
| kbbl | 620,200 | 110,200 |
| GBtu | 3,827,400 | 686,900 |
| Heating value, Btu/gal | 146,924 | 148,454 |
| S content | 0.99 | 1.42 |
| Equivalent $SO_2$ content, lb $SO_2$/MBtu | 1.08 | 1.54 |
| Gas | | |
| Total consumption | | |
| $Mft^3$ | 2,556,000 | 108,200 |
| GBtu | 2,602,200 | 117,000 |
| Heating value, $Btu/ft^3$ | 1,018 | 1,081 |

a. k = one thousand.
b. G = one billion.
c. M = one million.

Table 3. COMPARISON OF PROJECTED 1978 REGIONAL FOSSIL FUEL CONSUMPTION WITH HISTORICAL 1973 CONSUMPTION

| Geographic region[a] | Coal, ktons | Oil, kbbl | Gas, $Mft^3$ |
|---|---|---|---|
| Historical 1973 consumption | | | |
| New England | 1,080 | 82,930 | 6,070 |
| Middle Atlantic | 46,990 | 144,690 | 64,730 |
| East North Central | 135,960 | 23,340 | 105,590 |
| West North Central | 31,620 | 3,440 | 352,820 |
| South Atlantic | 75,860 | 141,380 | 202,660 |
| East South Central | 63,060 | 6,510 | 73,750 |
| West South Central | 4,730 | 20,850 | 1,957,070 |
| Mountain | 23,930 | 8,990 | 207,630 |
| Pacific | 3,740 | 76,970 | 451,220 |
| U.S. total | 386,970 | 509,100 | 3,421,540 |
| Projected 1978 consumption[b] | | | |
| U.S. total | 475,570 | 620,250 | 2,556,020 |

a. The states included in each geographic region are: New England - CT, ME, MA, NH, RI, VT; Middle Atlantic - NJ, NY, PA; East North Central - IL, IN, MI, OH, WI; West North Central - IA, KS, MN, MO, NE, ND, SD; South Atlantic - DE, DC, FL, GA, MD, NC, SC, VA, WV; East South Central - AL, KY, MS, TN; West South Central - AR, LA, OK, TX; Mountain - AZ, CO, ID, MT, NV, NM, UT, WY; Pacific - CA, OR, WA.

b. Regional consumption data not available.

projections indicate a general increase in the consumption of coal and oil, but a slight decrease in the consumption of gas. The regional increases or decreases are primarily influenced by fuel availability and price. In reviewing the data, it must be remembered that a significant amount of new generating capacity between 1973 and 1978 is from nuclear units. The data shown include the effect of projected decreases in fossil fuel utilization as a result of new nuclear units coming online as well as changes in fossil fuel consumption resulting from decreases in fuel availability of increases in cost.

The operating characteristics of all 800 U.S. power plants projected to be in operation in 1978 are outlined in Table 4. Also included in this table are the characteristics of the plants projected to operate out of compliance in 1978. As the data in the table indicate, 187 power plants out of a total of 800 were calculated to be out of compliance. It should be noted that many of the plants estimated to be out of compliance are likely implementing compliance plans that are different from those selected for this study. Even though plants out of compliance make up only 32% of the total population with respect to capacity, they burn about 50% of the total coal; only 20% of the total oil, and only 5% of the total gas. Plants out of compliance have a 30% higher S content in the coal burned and a 43% higher S content in the oil burned than the overall nationwide average. The average boiler size for plants out of compliance was about 30% greater than the average for all plants. The age range of boilers, the range of boiler sizes, and boiler capacity factor for plants out of compliance were not significantly different than the industrywide values.

## Byproduct Acid from Smelters

The 14 smelters located in the 11 Western States were analyzed separately from the 14 smelters in the 37 Eastern States of the U.S. The model assumes that existing S-burning acid plants and byproduct acid plants associated with smelter operations were operating at an equilibrium position in the 1975 market year. The model then addresses the incremental acid that is projected to be produced at both existing and new smelter locations in 1978. The 1978 incremental production estimated for the Western States amounted to 849,000 tons of acid. The analysis for smelters located in the Eastern States amounted to 811,000 tons of acid.

Part of the acid produced by western smelters was distributed in the East. This surplus western acid was marketed in the simulation model through transshipment terminals supplied by unit trains. The terminal locations included Chicago, Illinois; St. Louis, Missouri; Memphis, Tennessee; Baton Rouge, Louisiana; and Houston, Texas. Two additional transshipment terminals were added in the model at Buffalo, New York, and Detroit, Michigan, in order to analyze the marketing of 200,000 tons of byproduct acid from smelters in Canada. This concept is presented graphically in Figure 5.

## Byproduct Acid from Power Plants

The clean fuel alternative is defined as the incremental additional price for fuel that will meet the applicable $SO_2$ emission regulation. The ACFL selected for the model runs ($0, $0.35, $0.50, and $0.70/MBtu) were chosen to show the effect on potential volume of abatement acid. For some power plants with multiple boiler installations a mix of alternative methods produce the least-cost compliance strategy. A summary of the distribution of compliance strategies selected by the model for each ACFL model run is listed as follows:

Table 4. POWER PLANT OPERATING CHARACTERISTICS PROJECTED FOR 1978

| | 1978 all U.S. plants | 1978 plants out of compliance |
|---|---|---|
| No. of power plants | 800 | 187 |
| No. of boilers | 3,382 | 833 |
| Total capacity, MW | 411,000 | 132,600 |
| Total fuel coal, ktons[a] | 475,600 | 226,800 |
| GBtu[b] | 10,408,300 | 5,125,100 |
| Oil, kbbl | 620,300 | 110,200 |
| GBtu | 3,827,400 | 686,900 |
| Gas, Mft$^3$ [c] | 2,556,000 | 108,200 |
| GBtu | 2,602,200 | 167,000 |
| Average S content of coal, % | 2.12 | 2.81 |
| Oil, % | 0.99 | 1.42 |
| Emissions equivalent tons $H_2SO_4$ | | |
| Total emitted | 29,552,100 | 17,562,300 |
| Required abatement | 9,912,600 | 9,912,600 |
| Average capacity factor, % | 31.87 | 35.12 |
| Average boiler generating capacity, MW | 122 | 159 |
| Age of boilers, % | | |
| 0-5 | 5 | 10 |
| 6-10 | 8 | 10 |
| 11-15 | 8 | 6 |
| 16-30 | 42 | 42 |
| >30 | 37 | 32 |
| Size of boilers, % | | |
| <200 | 82 | 75 |
| 200-500 | 11.7 | 15 |
| 501-1000 | 6 | 9 |
| >1000 | 0.3 | 1 |
| Capacity factor of boilers, % | | |
| <20 | 40 | 35 |
| 20-40 | 20 | 17 |
| 41-60 | 23 | 29 |
| >60 | 17 | 19 |

a. k = one thousand.

b. G = one billion.

c. M = one million.

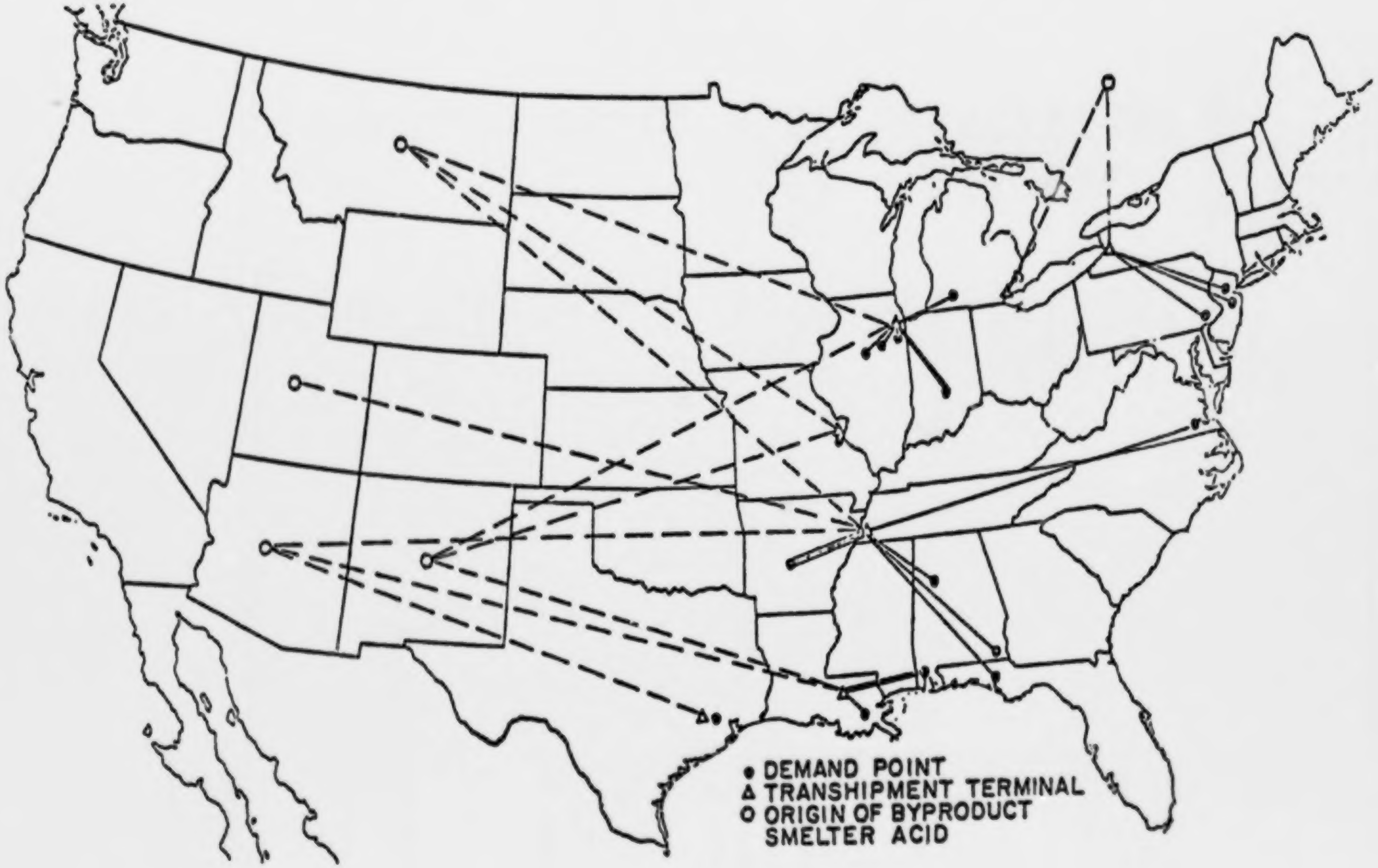

Figure 5. Geographic distribution of assumed supply and demand for western and Canadian acid at zero ACFL model run.

| Compliance strategy | ACFL, cents/MBtu<br>0 | 35 | 50 | 70 |
|---|---|---|---|---|
| Plants using clean fuel only | 187 | 168 | 113 | 71 |
| Plants using only limestone scrubbing | 0 | 7 | 41 | 77 |
| Plants using limestone scrubbers and clean fuel | 0 | 4 | 7 | 10 |
| Plants using MgO scrubbing only | 0 | 8 | 24 | 29 |
| Plants using MgO scrubbing and clean fuel | 0 | 0 | 2 | 0 |
| Total power plants | 187 | 187 | 187 | 187 |

The potential production and marketing of abatement acid for power plants that produced acid in each of the model runs are outlined as follows:

|  | ACFL, cents/MBtu<br>0 | 35 | 50 | 70 |
|---|---|---|---|---|
| No. of plants | 0 | 8 | 26 | 29 |
| Thousands of tons marketed | 0 | 2554 | 5108 | 5559 |

Power plants that were the best candidates for production of byproduct acid were generally larger, newer plants with high load factors. The distinctive characteristics were (1) most boilers less than 10 yr old, (2) average size about 600 MW (less than 15% smaller than 200 MW), and (3) the average capacity factor about 60%. The average load factor for potential acid-producing plants was more than three times as high as the average for all plants considered.

A summary of the compliance strategies developed from the model runs for controlling excess emissions projected for 1978 is outlined in the following tabulation:

Strategies Selected for Reducing Emissions

(Reductions expressed as equivalent thousands of tons of $H_2SO_4$/yr)

| ACFL, cents/MBtu | By using clean fuel | Total by scrubbing | By MgO scrubbing | By limestone scrubbing | Total reduction |
|---|---|---|---|---|---|
| 0 | 9,912 | 0 | 0 | 0 | 9,912 |
| 35 | 7,993 | 2,885 | 2,554 | 330 | 10,878 |
| 50 | 3,123 | 9,503 | 5,108 | 4,395 | 12,627 |
| 70 | 700 | 12,583 | 5,595 | 6,988 | 13,284 |
| ∞ | - | 13,598 | - | - | 13,598 |

## Equilibrium Solution

A summary of model results for smelter and power plant sales to acid plant demand points for all model runs is outlined in Table 5. These results show the potential quantity of power plant acid in relation to the total market. At the \$0.70/MBtu ACFL, the potential for production of acid (abatement capacity) at a cost below the alternative clean fuel premium fuel cost exceeded the market demand (sales) for the acid by 5 million tons. The plants that would not be able to market the acid used limestone scrubbing even though production of acid would have been less costly if markets were available. At the \$0.35/MBtu level, essentially all of the acid that could be produced economically compared to purchase of complying fuel was sold. The small differential in sales between the \$0.50 and \$0.70/MBtu level of ACFL indicates that the market for byproduct acid from power plants was nearly saturated at 5 million tons, or approximately 15% of the total market. Further substitution of byproduct acid in the existing market would depend on substantial increase in the price of S; \$60 was assumed for the study.

## Distribution of Acid Markets

Distribution of acid for the 90 acid plants considered in each model run is outlined as follows:

| | ACFL, cents/MBtu | | | |
|---|---|---|---|---|
| | 0 | 35 | 50 | 70 |
| Producing from S | 58 | 42 | 30 | 28 |
| Buying from smelters only | 21 | 11 | 1 | 5 |
| Buying from steam plants only | 0 | 22 | 41 | 41 |
| Producing from S and buying from smelters | 11 | 6 | 2 | 1 |
| Producing from S and buying from steam plants | 0 | 2 | 3 | 2 |
| Producing from S and buying from smelters and steam plants | 0 | 0 | 0 | 1 |
| Buying from smelters and steam plants | 0 | 7 | 13 | 12 |
| Total acid plants | 90 | 90 | 90 | 90 |

Four significant factors that affect the purchase of abatement acid by current producers of $H_2SO_4$ in this study are listed as follows:

1. Size
2. Age
3. Compliance with clean air standards
4. Location

Abatement acid produced in the model run from the utility industry at the \$0.70/MBtu clean fuel premium was distributed to 56 different demand points in 23 states. The current supply that was replaced by byproduct acid was generally from

Table 5. SUMMARY OF MODEL RESULTS FOR SMELTERS AND POWER PLANT SALES TO ACID PLANT DEMAND POINTS

(Thousands of tons of $H_2SO_4$)

| | ACFL, cents/MBtu | | | |
|---|---|---|---|---|
| | 0 | 35 | 50 | 70 |
| Eastern smelters | | | | |
| Capacity | 818 | 818 | 818 | 818 |
| Sales | 818 | 818 | 818 | 818 |
| Demand points | 15 | 13 | 12 | 14 |
| Western smelters | | | | |
| Capacity | 738 | 738 | 738 | 738 |
| Sales | 738 | 738 | 594 | 498 |
| Demand points | 15 | 8 | 3 | 3 |
| Canadian acid | | | | |
| Capacity | 200 | 200 | 200 | 200 |
| Sales | 200 | 200 | 200 | 200 |
| Demand points | 4 | 4 | 2 | 3 |
| Total smelter acid capacity | 1,756 | 1,756 | 1,756 | 1,756 |
| Sales | 1,756 | 1,756 | 1,612 | 1,516 |
| Demand | 32[a] | 24[a] | 16[a] | 19[a] |
| Mixed demand points | 11 | 13 | 15 | 13 |
| Steam plants | | | | |
| Capacity | - | 2,635 | 8,497 | 10,758 |
| Sales | - | 2,554 | 5,108 | 5,595 |
| Demand points | - | 31[a] | 57[a] | 56[a] |
| Mixed demand points | - | 9 | 16 | 14 |
| Port Sulphur to $H_2SO_4$ plants | | | | |
| Capacity | 32,237 | 32,237 | 32,237 | 32,237 |
| Sales | 30,481 | 27,926 | 25,516 | 25,126 |
| Demand points | 69[a] | 50[a] | 35[a] | 31[a] |
| Mixed demand points | 11 | 8 | 5 | 4 |
| Port Sulphur only | 58 | 42 | 30 | 28 |

a. Steam plants and Eastern and Western smelters can supply a common demand point.

smaller, older plants remotely located from the elemental S production points on the Gulf Coast. The larger, more efficient plants generally can produce acid at costs lower than the delivered cost of abatement byproducts. However, there are exceptions Savings in transportation cost because of location advantage can offset production co differential.

## Sensitivity Analyses

One of the key inputs in the analysis of the potential market for abatement byproduct acid is the price of elemental S. All the results of this study are based on S price of \$60/long ton f.o.b. Port Sulphur. A \$20.00 decrease in the unit price of S lowers the avoidable cost of production for $H_2SO_4$ at each respective acid plant by \$6.11/ton of acid produced. This price structure would reduce the quantity of both byproduct smelter acid as well as the abatement acid from power plants that can be marketed in the model.

The model assumed distribution of byproduct acid by rail shipment. Since several of the potential producers are located on navigable waterways, barge transportation could be used. As an example of possible savings on shipment costs, estimates were made for barge shipments of selected production totaling 700,000 tons. The cost differential between rail and barge transportation totaled \$725,000 or about \$1/ton of acid. This potential savings is 11% of the average transport cost. Because barge rates are normally negotiated, rates were not available for inclusion in the transportation model. An in-depth analysis will be required before realistic conclusions can be made.

## RECOMMENDATIONS

Information on current compliance programs for existing power plants and for additional planned capacity was not available during the period of this study. The results of the work show that the potential for use of recovery technology is good and the initial follow-on work should focus on plants where compliance alternatives are still flexible. A survey of compliance plans should be carried out and the option of producing byproduct acid should be evaluated by incorporating specific information on those plants into the program data base. This evaluation would be particularly helpful in the planning process for future coal-fired power plants or for those that may be required to convert from gas or oil to coal.

# FEASIBILITY OF GYPSUM PRODUCTION AND MARKETING AS AN ALTERNATE $SO_2$ EMISSION CONTROL STRATEGY FOR FOSSIL-FIRED POWER PLANTS

The passage of the Clean Air Act in 1967 and the various amendments have prompted increased efforts by government and industry to reduce pollutants in emissions from fossil-fired power plants. Stack-gas scrubbing processes for removal of $SO_2$ emissions have received the most attention. There are alternative systems of scrubbing for removal of $SO_2$ emissions; but the lime-limestone systems which absorb the $SO_2$ and convert it to solid compounds of calcium sulfites ($SO_3$) and sulfates ($SO_4$), which are then discarded, have been most widely applied by the industry. Those processes are called "throwaway" processes. In general, they are less expensive to install and operate than alternative scrubbing systems. The "throwaway" product has no economic value, is costly to discard, may create future problems of ground water pollution, and wastes S, a vital resource.

Processes recovering the $SO_2$ in useful form are potentially superior to the lime-limestone methods because they overcome the disadvantages associated with the "throwaway" systems. Before such systems will be put into use, however, there must be confidence that the useful byproduct will generate adequate sales revenue to offset additional cost, if any, of the alternative systems. EPA and TVA have conducted studies to evaluate the feasibility of marketing byproducts from $SO_2$ emission control. The design of the system(s) chosen is developed from available data, costs are estimated on a uniform basis, and potential markets are determined for the byproducts.

A major purpose of this study is to evaluate the existing wallboard products industry and cement industry as markets for abatement gypsum produced by an $SO_2$ emission control system. Gypsum-producing systems are in use on oil-fired boilers in Japan, and the resultant product is used successfully in wallboard manufacturing. A pilot operation is currently underway on a coal-fired facility in the U.S. Samples of the gypsum made there have been successfully used in wallboard manufacturing under commercial conditions.

The wallboard products manufacturing industry is currently the dominant user of gypsum. This market potential has been given major attention, but consideration has been given to potential uses in the cement industry. The major objectives of the study are:

1. To identify basic conditions of supply and demand for the gypsum industry.
2. To characterize demand and project growth in demand by major markets.
3. To identify potential problems in market entry and to suggest market strategies.
4. To evaluate costs for several different gypsum-producing FGD systems and to develop cost estimates for representative systems.
5. To further develop and improve an analytical model for conducting abatement product marketing investigations.
6. To apply the model to determine optimum strategies for the industry on a plant-by-plant basis and in total.
7. To suggest further research needs.

The study is approached in four sequential steps. The existing gypsum industry is analyzed first to determine the market potential for abatement gypsum. Specific quantities and costs are developed for each demand point and for the total industry. Next, the cost of $SO_2$ emission control by gypsum-producing processes is compared to the limestone throwaway system to determine a basis for the supply of abatement gypsum from which the total potential production and costs are calculated. Then the revenue based on the replacement of crude gypsum is determined and compared to calculated production costs. Specific plants are identified that have an economic incentive to control $SO_2$ emissions by gypsum production. Results, conclusions, and limitations are summarized in the final step.

## Major Assumptions

The study is conducted under the premise that all steam plants must operate in compliance with existing $SO_2$ regulations. It is assumed that use of low-S fuel is an available alternative to meet compliance. A premium cost of $0.70/MBtu heat input is assumed for complying fuel. Determination of actual premium value is beyond the scope of the study; the level chosen is a reasonable economic screen. Boilers are not considered to be candidates to install an FGD system when calculated cost of scrubbing exceeds $0.70/MBtu heat input. All remaining boilers are assumed to install the limestone throwaway system unless revenue from sale of abatement gypsum is adequate to offset or exceed the additional cost of the gypsum-producing $SO_2$ emission control system. Abatement gypsum is assumed to be interchangeable with natural gypsum in the manufacture of wallboard and cement. Revenue generated from sales of abatement gypsum is based on a projected quantity and delivered cost of crude gypsum to each currently existing demand point. Any demand point is assumed to purchase abatement gypsum if cost is equal to or less than estimated current delivered cost of crude gypsum.

## The Gypsum Industry

Gypsum is a naturally occurring nonmetallic mineral found in almost limitless deposits in many parts of the world. Reserves exist in many sections of the U.S. with the notable exception of coastal areas and the Southeast. Crude gypsum consumed in the areas without natural reserves is mostly imported from Canada. Imports historically account for 35 to 40% of our domestic needs.

Gypsum is a low-value product since mining costs are low. Variable costs of mining were estimated for purposes of this study at $3/ton for domestic mines and $2/ton in Canada. The costs are estimated to be lower in Canada because the quality of reserves is generally better than in the U.S. Mining costs vary between regions and by type of mining method used; however, differences could not be quantified.

Domestic gypsum consumption is highly variable and follows the fortunes of the building industry. The year 1973 was a record for the gypsum industry in the U.S. when consumption amounted to over 20 million tons. Domestic production was 13,558,000 tons with an average reported mine value of $4.18/ton.[2] Imports amounted to 7,661,000 tons with an average reported mine value of $2.30/ton. Three major markets exist for crude gypsum: (1) the wallboard products industry, 71%; (2) the cement industry, 20%; and (3) agriculture, 8%. According to long-range projections made by BOM, gypsum use is expected to grow at an annual rate of 1.5 to 2.0%.

Growth is expected in each of the major markets. In addition, the mobile home industry may develop into a new market for wallboard as a result of recent changes in building codes.

The wallboard products portion of the industry is both highly concentrated and highly integrated from mining through wallboard manufacture. Entry barriers, now rated high, could be lowered if abatement gypsum does become available. Entry barriers are high partly because the firm must control reserves as well as manufacturing plants. In areas where reserves are not available, the firm normally owns or contracts foreign reserves and attendant facilities to enable ocean transport at minimum cost. If abatement gypsum were available, the wallboard plant would be the only capital investment required to enter the industry.

Most of the gypsum used in the cement industry is purchased from the open market rather than being supplied from captive mines. Cement plants are widely scattered and shipping costs add significantly to delivered costs. Therefore, the logistics and market entry conditions would favor sales of byproducts to the cement industry.

Data bases are developed for the wallboard products industry and the cement industry. The data bases include an estimate of projected gypsum use in 1978 at each wallboard plant and each cement plant based on use in 1973 (the year of maximum consumption). The data bases also include estimated minimum delivered cost of crude gypsum to each demand point. Delivered costs to wallboard plants are based on estimated variable mining cost of \$3/ton f.o.b. domestic mine or \$2/ton f.o.b. foreign mine. In each case, the company-owned mine was considered the supply point for the wallboard plant. The price to the cement industry is based on the current value of crude gypsum used in the cement industry estimated at \$6/ton f.o.b. mine. The two-price system is used because gypsum for wallboard product plants is supplied from captive mines at a lower cost than gypsum for cement.

There is little precedent to draw upon to predict how present crude gypsum producers would react in pricing their product to compete with abatement gypsum. All wallboard producers own or contract their own supplies of crude gypsum. These producers also supply gypsum requirements of the cement industry in an open market.

It is assumed that the integrated producers would continue to mine and distribute crude gypsum to their wallboard plants as long as they met variable cost of mining as estimated above. Since gypsum sales to the cement industry are made in an open market, gypsum producers would be reluctant to lower existing market prices on all crude gypsum sales to compete with localized production of abatement gypsum. For these reasons, the two-price system is used in the major portion of the analysis. Other price situations are also evaluated and reported.

This data base provides total tonnage and revenue potential for abatement gypsum in existing markets. Only three steam plants in the western U.S. were found to be candidates to install an FGD system. These three plants are located near gypsum-producing areas. For practical purposes, therefore, the gypsum-producing alternative is not a viable or important alternative for steam plants in the West. The analysis that follows is limited to the eastern U.S.

Projected consumption in 1978 in the eastern U.S. is 15,043,301 tons. Fifty-five wallboard plants and 132 cement plants are located in this area. Wallboard plants will consume an estimated 11,855,910 tons and cement plants 3,187,391 tons. Total imports will amount to 5.9 million tons. Wallboard plants will consume 4.8 million tons, and cement plants will consume 1.1 million tons of imported material. The total delivered cost of gypsum to demand points in 1978 is estimated at

$124,400,000 with an average value per ton of $8.27. This represents the maximum revenue potential to the utility industry from sales of abatement gypsum in 1978.

## FGD Cost Comparisons

Three gypsum-producing FGD systems--limestone-gypsum, Chiyoda Thoroughbred 101, and Dowa aluminum sulfate /$Al_2(SO_4)_3$_7--were chosen to be evaluated in this study. In addition, costs for the limestone slurry throwaway system originally developed by TVA are updated to the same base conditions. A brief description of each process follows:

1. Limestone slurry process. Downstream of an electrostatic precipitator (ESP) which is used for particulate removal, stack gas is washed in a mobile-bed absorber with a recirculating slurry of limestone and reacted calcium salts to remove $SO_2$. Limestone feed is wet ground prior to addition to the absorber effluent hold tank. $CaSO_3$ and $SO_4$ salts are withdrawn to a disposal area for discard. Cleaned gas from the absorber is reheated to 175°F before exiting the stack. Design is based on data taken from the EPA-TVA-Bechtel Shawnee test program.

2. Limestone/gypsum process. Particulate and $SO_2$ removal is accomplished in the same manner as in the limestone slurry process. A bleed stream from the absorber is fed to a neutralization reactor where it is contacted with 98% $H_2SO_4$ to convert excess $CaCO_3$ in the slurry to $CaSO_4 \cdot 2H_2O$ and to lower the pH of the stream to approximately 4.0-4.5 to facilitate downstream oxidation. The reaction product is fed to a high-pressure oxidizer where $CaSO_3$ in the slurry is contacted with air to form $CaSO_4$. The gypsum product is dewatered by thickener and belt filter and conveyed to a storage area. The process (based on Mitsubishi technology) is a conceptual design developed by TVA to be used for comparison with other gypsum-producing processes.

3. Chiyoda 101 process. After particulate removal in an ESP, gas is contacted with a dilute (2-3%) $H_2SO_4$ solution in a specially designed absorber-oxidizer vessel to convert $SO_2$ to $H_2SO_4$. Rich liquor is withdrawn from the absorber and reacted with a limestone slurry in a Chiyoda-designed crystallizer to form gypsum. Limestone feed is wet ground prior to addition to the crystallizer. Overflow from the crystallizer is clarified and returned to the absorber as scrubbing liquor. The gypsum product is dewatered by rotary drum filter and conveyed to a storage area. The process has been developed by Chiyoda Chemical Engineering and Construction Company, Ltd., Yokohama, Japan.

4. Dowa process. Following an ESP for particulate removal, stack gas is contacted in a mobile-bed absorber with an $Al_2(SO_4)_3$ solution to remove $SO_2$. A bleed stream from the absorber is contacted with air in an oxidizer to convert aluminum sulfite /$Al_2(SO_3)_3$_7 to $Al_2(SO_4)_3$. The $Al_2(SO_4)_3$ is reacted with limestone in neutralizing tanks to form the gypsum product and regenerate scrubbing liquor which is recycled to the absorber. Limestone feed is wet ground prior to addition to the neutralizing tanks. The gypsum product is dewatered by thickener and drum filter and conveyed to a storage area. The process has been developed by the Dowa Mining Company, Ltd., Tokyo, Japan.

Design and economic factors chosen to provide a consistent base for comparison of the processes are defined below:

1. Project schedule and location. Project assumed to start in mid-1975 with a 3-yr construction period ending mid-1978. Average cost basis for scaling, mid-1977; startup mid-1978. A midwestern plant location is assumed.

2. Power unit size and status. Costs are projected for a 500-MW new power unit. Heat rate is 9,000 Btu/kWh. New units are designed for a 30-yr life, 127,500 hr of operation.

3. Fuel type. Coal assumed for this study is bituminous--12,000 Btu/lb, 12% ash, 3.5% S (dry basis).

4. Particulate removal and disposal. A 99.5% efficient ESP has been assumed. Cost of particulate removal and disposal is not included in the economic evaluation.

5. $SO_2$ removal. 90% removal is specified as the base value.

6. Sludge disposal. Pond for the disposal of sludge from the limestone slurry process is located 1 mi from power plant. Water balance is based on closed-loop operation.

7. Capital charges. Regulated (profit and taxes included) economic basis is used. Revenue requirement estimates utilize a base value of 14.9% of fixed investment (10% cost of money).

8. System design assumed to be developed (not "first of kind"); no redundancy is included; only pumps are spared; experienced design and construction team is assumed to be utilized.

A summary of the revenue requirements for 7000 hr operation is presented in Table 6.

Table 6. SUMMARY--TOTAL ANNUAL REVENUE REQUIREMENTS

(Excluding credit for sale of abatement gypsum)

| FGD system | Total annual revenue requirements, $ | Mills/kWh | Cents/MM Btu heat input | $/ton coal burned | $/ton S removed | $/ton gypsum produced | Tons gypsum produced/yr |
|---|---|---|---|---|---|---|---|
| Limestone slurry | 10,105,300 | 2.89 | 32.08 | 7.70 | 281.64 | - | - |
| Limestone/gypsum | 12,098,100 | 3.46 | 38.41 | 9.22 | 337.18 | 50.21 | 240,960 |
| Chiyoda | 15,483,400 | 4.42 | 49.15 | 11.80 | 431.17 | 77.88 | 198,800 |
| Dowa | 10,472,200 | 2.99 | 33.25 | 7.98 | 291.62 | 52.53 | 199,360 |

a. Basis:
500-MW new coal-fired power unit.
3.5% S in coal.
90% $SO_2$ removal.
7,000 hr/yr operation.
Mid-1978 cost basis.
Onsite disposal of limestone sludge.

The Dowa process has the lowest cost of those estimated. However, the technology has not been fully developed for use on coal-fired boilers. The limestone-gypsum process costs are used as a basis for estimating production costs in the following sections.

## Potential Supply of Abatement Gypsum

Cost factors and premises developed in the base case estimates were applied to operating characteristics of each steam plant in the industry. Operating characteristics were taken from FPC data that had been supplied by the utilities. There were 187 plants calculated to be out of compliance. FGD costs were calculated for both the limestone scrubbing and the limestone gypsum processes for each plant. Based on the cost calculations, 116 plants are candidates to install an FGD system. The remaining 71 plants are assumed to purchase low-S fuel to meet compliance. Three plants were located in the West and are assumed to install the limestone slurry throwaway system. The remaining 113 plants are subjects of the market analysis.

Each of these plants is assumed to install the limestone slurry process unless revenue from gypsum sales can be predicted to offset or exceed added costs of the gypsum process. Total first-year cost to operate the limestone throwaway process is calculated at about $2 billion which includes depreciation and ponding costs. Over 25 million tons of Ca solids would have to be discarded.

Differential costs between the limestone and limestone-gypsum processes ranged from negative $13 to positive $20/ton of gypsum. Potential gypsum production is 27 million tons, almost twice the projected 1978 consumption in the Eastern States. Fifteen power plants could control $SO_2$ emissions by the gypsum process at a lower absolute cost than by the throwaway process. These plants could produce a total of 863,000 tons in the first year. An additional 25 plants can meet compliance by producing gypsum at incremental cost of up to $3/ton (the estimated cost of mining crude gypsum). These 25 plants could produce 3.6 million tons.

Negative or low incremental costs of the gypsum process are shown to occur at new plants where annual $SO_2$ removal requirements are low. All negative costs were associated with relatively new plants that would produce less than 100,000 tons of gypsum annually.

## Results of Market Model

A modified linear programing model is used to calculate revenue from abatement gypsum sales to each steam plant. The model is based on the premise that FGD systems are mutually exclusive and that both limestone and limestone-gypsum systems will not be installed at the same plant. Gypsum production will be either zero tons or the maximum to be produced at compliance. Gypsum will only be produced and supplied when revenue can be predicted to offset added production cost.

The market analysis is conducted and presented in a series of scenarios with progressively more stringent restrictions to predict the number of plants that would choose the gypsum alternative. Each scenario is developed in the same manner that a specific steam plant might employ to determine market potential for the individual plant. Restrictions are developed to predict the steam plants which could lower cost of compliance by producing and marketing abatement gypsum if all plants were to enter the industry in 1978.

The analysis was conducted in such a manner that savings to the gypsum users could be calculated along with lowered cost of compliance to the utility industry. The final market solution predicted that 30 steam plants could lower cost of compliance by producing and marketing gypsum; the locations are shown in Figure 6. These 30 plants would serve a total of 93 demand points. The location of demand points is shown in Figure 7. Only one wallboard plant would purchase abatement gypsum (partly because cement plants offer a higher price outlet). Compliance cost would be reduced in the first year by $11 million to the 30 power plants compared to use of limestone scrubbing. This amounts to an average savings of over $350,000/plant. In terms of total industry cost of compliance, the savings by gypsum production would amount to less than 1%. Savings to the gypsum industry are calculated to equal $1 million. Total gypsum production is 2.4 million tons with an average production of 80,000 tons/plant. The total is approximately 53% of the amount that could be produced and sold (at $3/ton) with costs lower than limestone scrubbing.

Abatement gypsum would be purchased by 92 cement plants. Abatement gypsum would replace 67% of the projected use of crude gypsum by cement plants. Cement plants were projected to import 1.1 million tons. Production from the 30 steam plants would replace 74% of the imported material used in cement plants.

Use of gypsum-producing technology at the 30 power plants would solve only 8.7% of the electric utility $SO_x$ compliance problem and reduce the required ponding of Ca solids by 8.0%.

The market model was also used to assess the feasibility of gypsum production and marketing assuming that wallboard plants were the only effective market outlets for abatement gypsum. Under this condition, only nine utilities could reduce compliance costs by producing and marketing abatement gypsum to the wallboard industry. These 9 plants could produce and market a total of 608,000 tons of abatement gypsum on an average of 67,500 tons/plant. Total reduction in compliance cost for the 9 plants in comparison to the limestone throwaway system would amount to $1.6 million or an average of $184,000/plant. The reason that the wallboard market is so limited is that existing plants are built at the same location as the gypsum mine or at the point of minimum water transportation costs. Cement plants, on the other hand, are not located at gypsum mines and a high percentage of the cost of crude gypsum is transportation cost rather than product cost.

An analysis was conducted based on a $3/ton price reduction to cement plants. Under this lower price assumption, 27 utilities could still reduce compliance costs by producing and marketing abatement gypsum. This compares to 30 utilities found under conditions projected for 1978. The reduction in abatement gypsum sold would amount to 365,000 tons. Under the reduced price assumption, the major difference in outcome of the analysis was that savings in compliance cost for power companies was reduced from $11 million to $6.2 million.

## Conclusions

1. Because of huge reserves, no major national interest would be served by subsidizing abatement production to serve as a stockpile for later use.

2. Gypsum production and marketing offers a limited potential to the utility industry to lower cost of compliance; only about 8% of the electric utility compliance problem would be solved by this method. Production cost relative to throwaway use of limestone scrubbing is too great for large plants which

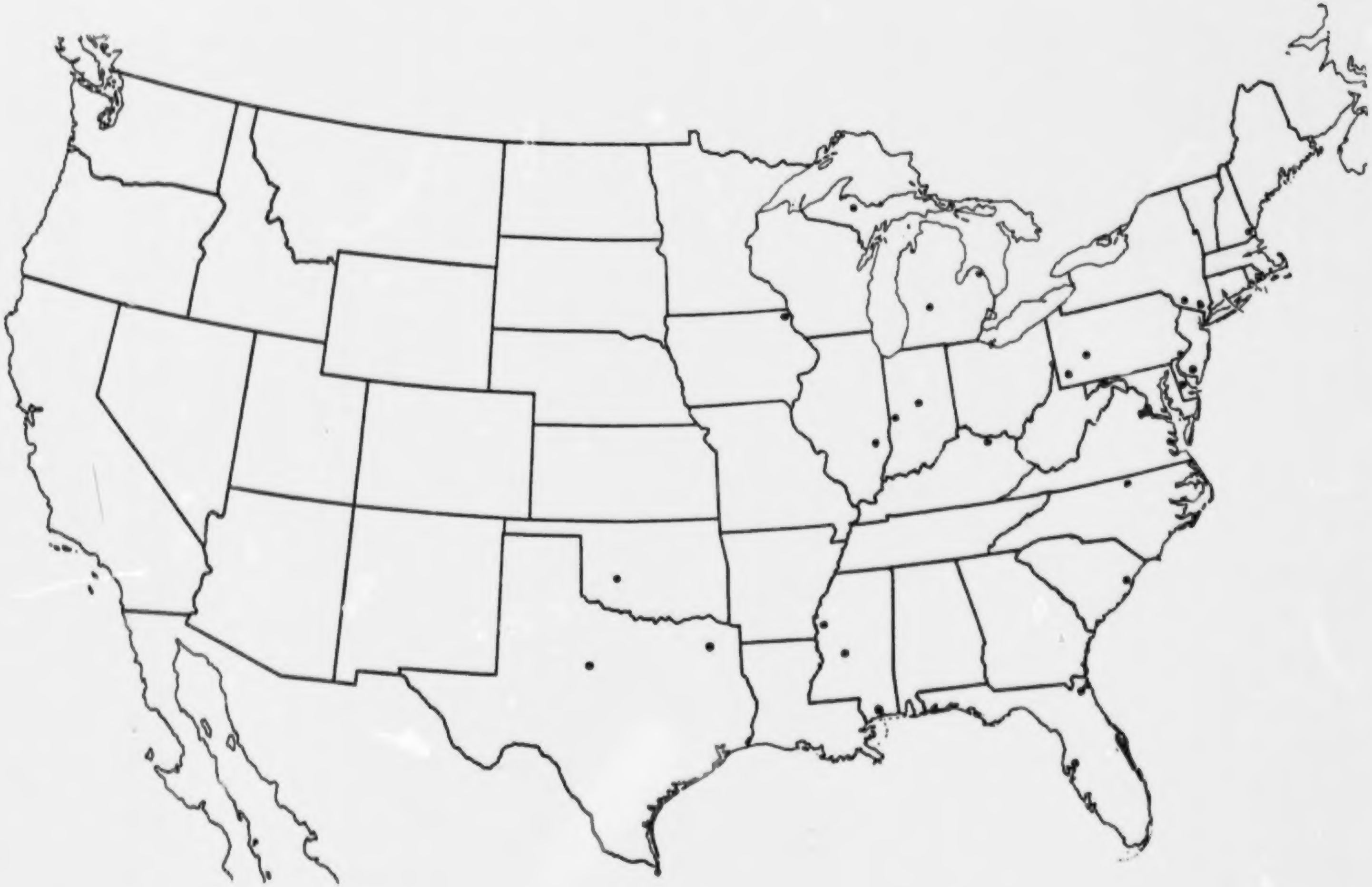

Figure 6. The locations of steam plants that could lower cost of compliance by producing and marketing gypsum.

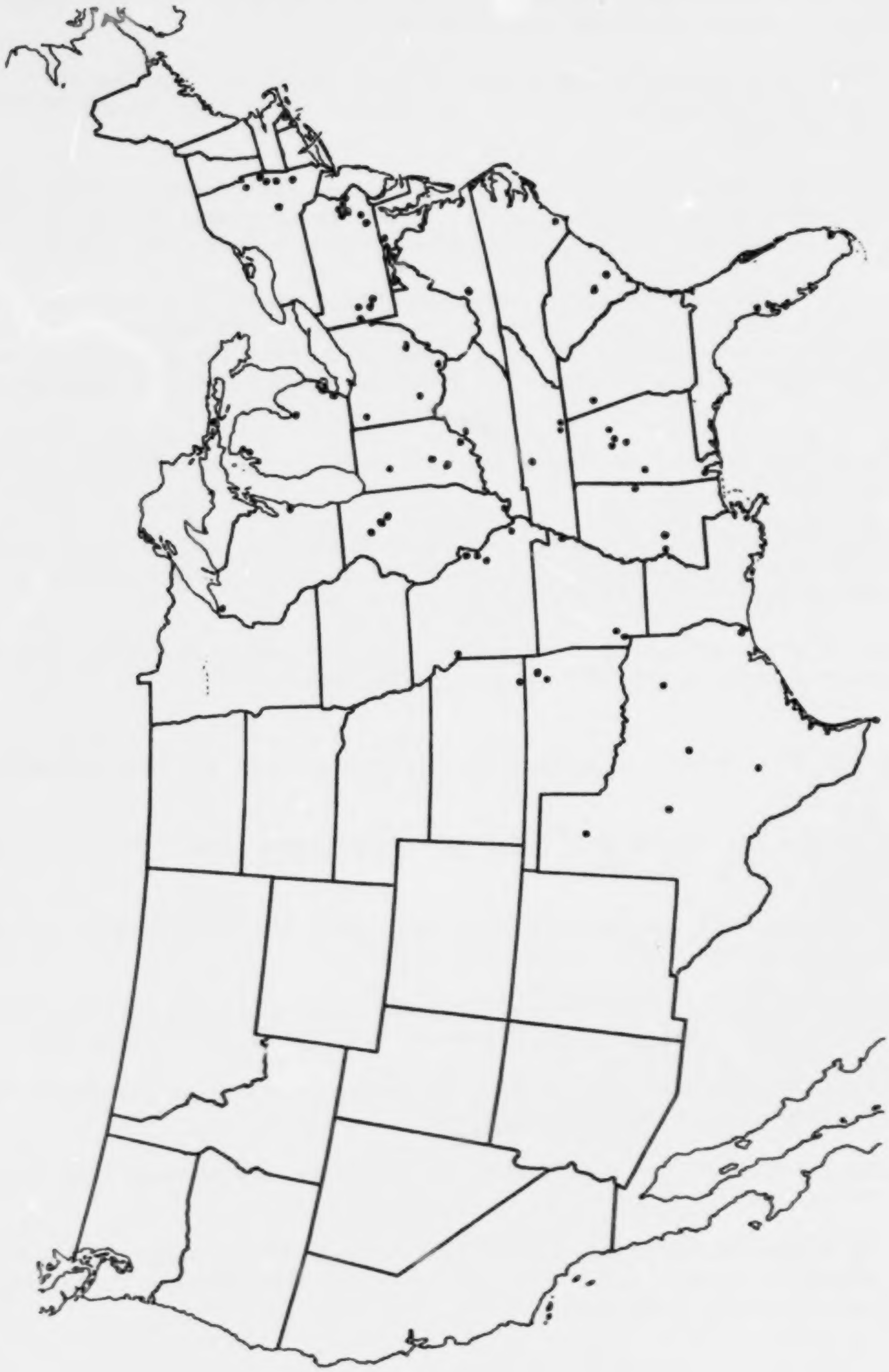

Figure 7. Location of demand points for byproduct gypsum produced by steam plants.

contribute the major share of $SO_2$ emissions. Incremental cost of producing gypsum is greater than the estimated mining costs for natural gypsum on approximately 85% of total possible abatement production. Only about half of the gypsum that could be produced and sold (at a price of $3) with costs lower than limestone scrubbing was marketed.

3. Gypsum production and marketing appear to be a viable alternative for relatively new plants where required $SO_2$ removal amounts to 20,000-30,000 tons of S annually.

4. When viewed in a total program of byproduct production and marketing, gypsum takes on added significance in that it is particularly well suited to the segment of the industry with a small annual volume of required S removal.

5. Cement plants offer the greatest potential market outlet for abatement gypsum; the wallboard industry would provide an extremely limited market. The demand at cement plants averages 25,000 tons/plant and offers the possibility for about 30 steam plants to locate a few local market outlets for abatement gypsum.

6. Abatement gypsum appears to offer fewer problems in the manufacture of cement than in wallboard.

7. Price reaction by gypsum producers cannot be predicted, but 27 steam plants would be predicted to continue to produce and market abatement gypsum to the cement industry in the face of a $3/ton price reduction.

8. Stability of the solution may be further ensured since such a high proportion of abatement market is gained by replacing imported gypsum.

In addition to the findings generated by the study, other specific accomplishments may be cited.

1. Specific supply and demand data bases for crude gypsum were established and may be maintained or improved.

2. A computerized system for approximating rail rates was developed in conjunction with the study series and is being maintained.

3. Operating characteristics at the boiler level were projected for each fossil-fired power plant in the U.S. and placed in a data base for future use.

4. A computer model was developed to test for compliance and to calculate FGD costs for a number of alternative systems.

5. Procedures and models were established to calculate net revenue from sales of byproducts from steam plants.

6. Support is being generated to maintain and improve on the work developed to use the models to assist individual utilities in their efforts to develop appropriate plans for compliance.

## Limitations

The analysis was conducted under the assumption that abatement gypsum is interchangeable with crude gypsum for use in wallboard and cement. Both advantages and disadvantages are likely. Tests under plant conditions, particularly in cement manufacture, need to be conducted to quantify cost associated with the use of abatement gypsum. Further work to quantify the supply price of crude gypsum of producing areas is needed. The use of estimated average costs for all regions detracts from the accuracy of results but probably does not affect the conclusions. In that regard, gypsum industry cost information is not generally available; it is difficult for a researcher outside the industry to develop the intimate knowledge of the industry required for in-depth analysis. This study should serve to establish potential, but specific studies need to be conducted for each potential producer to more accurately determine actual cost and revenue opportunities.

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# REGENERABLE PROCESSES SESSION

Session Chairman

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Research Triangle Park, North Carolina

# STATUS REPORT ON THE WELLMAN-LORD/ALLIED CHEMICAL FLUE GAS DESULFURIZATION PLANT AT NORTHERN INDIANA PUBLIC SERVICE COMPANY'S DEAN H. MITCHELL STATION

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## ABSTRACT

The Northern Indiana Public Service Company and the U.S. Environmental Protection Agency entered into a cost-shared contract in June of 1972 for the design, construction, and operation of a regenerable flue gas desulfurization (FGD) demonstration plant. The system selected for the project was a combination of the Wellman-Lord $SO_2$ Recovery Process and the Allied Chemical $SO_2$ Reduction Process. The FGD plant was to be retrofitted to NIPSCO's 115 MW pulverized coal-fired Unit No. 11 at the Dean H. Mitchell Station in Gary, Indiana. NIPSCO entered into contracts with Davy Powergas, Inc., for the design and construction of the FGD plant and with Allied Chemical Corporation for operation of the plant.

Construction has now been completed and the FGD plant acceptance test was successfully completed on September 14, 1977. The plant is presently beginning a 1-year demonstration test period during which information will be collected and reported regarding pollution control performance, secondary effects, economics, and reliability of the system.

## Introduction

In June 1972, the Northern Indiana Public Service Company (NIPSCO) and the U.S. Environmental Protection Agency (EPA) reached agreement on a cost-shared contract for the construction of the Davy Powergas Wellman-Lord/Allied Chemical Flue Gas Desulfurization (FGD) Demonstration Plant to be retrofitted to NIPSCO's boiler No. 11 at the Dean H. Mitchell Station in Gary, Indiana. The integrated Davy Powergas Wellman-Lord $SO_2$ recovery/Allied Chemical $SO_2$ reduction process was selected because it met NIPSCO's need to evaluate a technology for meeting State and Federal $SO_2$ emission limitations while avoiding the use of scarce and expensive land for sludge disposal, and it met EPA's need to demonstrate a regenerable FGD process capable of byproducing elemental sulfur. In addition, the Wellman-Lord/Allied Chemical FGD plant showed great promise for successful integrated operation since each of the two processes had proven successful in several separate applications. The Wellman-Lord $SO_2$ recovery process had operated reliably and with high $SO_2$ removal efficiencies in oil-fired utility applications, in sulfuric acid plants, and in petroleum refineries. The Allied Chemical $SO_2$ reduction process had operated well in smelter applications in which the sulfur loading far exceeded that expected from NIPSCO's boiler No. 11.

The cooperative NIPSCO/EPA project to demonstrate the Wellman-Lord/Allied Chemical FGD plant was subdivided into three phases: Phase I--Design Engineering and Cost Estimation; Phase II--Construction, Shakedown Operation, and Acceptance Testing; Phase III--Demonstration Test Year. NIPSCO subcontracted responsibility for Phase I to Davy Powergas, Inc., the developer and vendor of the Wellman-Lord $SO_2$ recovery process. Davy Powergas was also responsible for construction of the FGD plant and for startup and operation of the complete system until Acceptance Testing was successfully concluded. Allied Chemical, under a separate subcontract to Davy Powergas, had responsibility for the basic design of the Allied Chemical $SO_2$ reduction section of the plant, and for startup assistance until Acceptance Testing was successfully concluded; in addition, Allied Chemical, under contract with NIPSCO, will operate the entire FGD plant throughout the demonstration test year.

To provide the data and information needed by potential users to evaluate the process' applicability in the utility industry, EPA employed the services of TRW, Inc., an independent test and evaluation contractor, to monitor and report the performance of the boiler and FGD plant during all periods of joint operation from shakedown test operation through the demonstration test year. The EPA/TRW test program includes three major tasks: (1) the boiler baseline test, (2) the acceptance test, and (3) the demonstration test. The boiler baseline test, conducted in 1974 and 1975, included chemical and physical characterization of the boiler flue gas and evaluation of the boiler's operating performance. The baseline test results, which established a basis for comparing boiler performance before and after retrofit of the FGD plant, were reported in February 1977. The acceptance test--a brief period of intensive testing during which the FGD plant had to meet stringent performance criteria before being "accepted" by NIPSCO from Davy Powergas--was initiated on August 29, 1977, and successfully concluded on September 14, 1977. A report of plant performance during the acceptance test period is scheduled for release in December 1977. The demonstration test began on September 16, 1977, and is scheduled to conclude on September 15, 1978. This joint NIPSCO/EPA demonstration of the Wellman-Lord/Allied Chemical FGD process will provide useful data and information on reliability and costs of the test system for comparison to other FGD processes and to other $SO_2$ emission control alternatives. A final project report, scheduled for release in late 1978, will include information on the pollution control performance, secondary environmental effects, reliability, and economics of the demonstration plant. This report, as well as interim data and information developed during the demonstration year, will be useful in the continuing evaluation of alternative techniques for controlling $SO_2$ and other pollutants from the combustion of fossil fuels.

## History of the Wellman-Lord/Allied Chemical Flue Gas Desulfurization Plant

As previously stated, the EPA/NIPSCO contract contained a scope of work which divided the project into three phases. Phase I covered the preparation of a process design manual and a capital and operating cost estimate. Phase II covered detailed engineering, procurement, and construction of the FGD unit. Phase III of the project involves the operation of the FGD unit for a 1-year period following the satisfactory completion of the acceptance test.

The original scope of work in the EPA/NIPSCO contract called for a period of performance for completion of Phases I, II, and III of 37 months from the effective date of the contract (June 30, 1972). The NIPSCO/Davy Powergas contract contained an estimated period of performance for completion of Phase II of 119 weeks, starting May 24, 1973, and ending September 5, 1975.

Phase I of the project was completed by Davy Powergas on November 30, 1972. The EPA and NIPSCO conducted a review of the process design manual and the capital and operating cost estimates. On January 21, 1973, NIPSCO authorized Davy Powergas to proceed with Phase II advanced engineering without final commitment on capital equipment. After extensive review of the capital cost estimate by all parties involved, agreement was reached on a contract ceiling cost and Davy Powergas was given full release on Phase II of the project on May 24, 1973.

Field mobilization for construction started on August 5, 1974, and the civil subcontractor started work on August 29, 1974. The civil package construction activities were completed during December 1974. The mechanical/general subcontractor started field mobilization on March 31, 1975.

A Unit No. 11 scheduled outage began on October 24, 1975, for duct work and utility piping tie-ins. These tie-ins were completed and Unit No. 11 was restarted on December 5, 1975.

Unit No. 11 flue gas was first introduced to the FGD plant booster fan and absorber on July 19, 1976, and the FGD plant reduction system preheat was first started on July 23, 1976.

Project delays through the construction phase were caused by accelerated cost escalation, extended contract negotiations, delays in design engineering due to process changes, extended deliveries on equipment and material, fabrication errors and delayed deliveries on prefabricated pipe, an absorber fire during construction, and adverse weather conditions.

## Preacceptance Test Operation

Following the first introduction of flue gas to the FGD plant booster fan and absorber on July 19, 1976, there were numerous shutdowns and startups of the FGD plant due to a wide variety of reasons. Many of the shutdowns were related to problems normally encountered in the startup of a major industrial plant. Other shutdowns were due to operational problems which occurred on Unit No. 11.

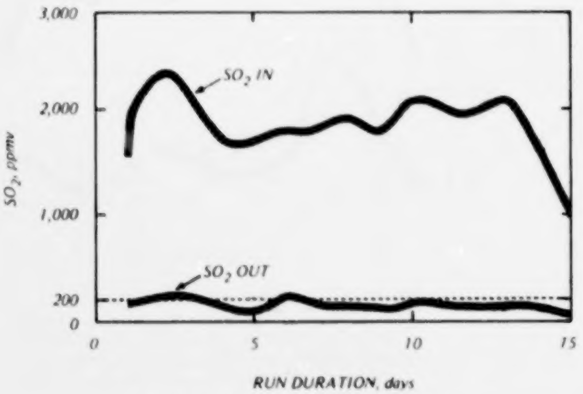
During the preacceptance test operating period of the FGD unit, there were three periods of sustained operation of the $SO_2$ recovery section of the plant:

| Run no. | Duration | Period |
|---|---|---|
| 1 | 15 days | Sept. 25 through Oct. 9, 1976 |
| 2 | 11 days | Oct. 13 through Oct. 23, 1976 |
| 3 | 14 days | Nov. 15 through Nov. 28, 1976 |

The $SO_2$ removal efficiencies achieved through these three periods of sustained operations are shown in figures 1 through 3.

During these periods the booster fan was operated at a fixed rate of 320,000 acfm (8,960 $m^3$/min) (the 92 MW design level) to simulate performance test conditions, while the load on Unit No. 11 fluctuated from 60 MW to 108 MW. The multileaf stack damper was open during these operating periods and, at times, allowed flue gas from Unit No. 6 to be pulled across the stack to the absorber.

The purge treatment section of the plant was inoperable during most of these operating periods.



THE $SO_2$ CONCENTRATION CURVES HAVE BEEN EXTRAPOLATED THROUGH DAYS 3 AND 5 BECAUSE OF INOPERATIVE INSTRUMENTATION.

Figure 1. Inlet and outlet $SO_2$ concentrations during run no. 1.

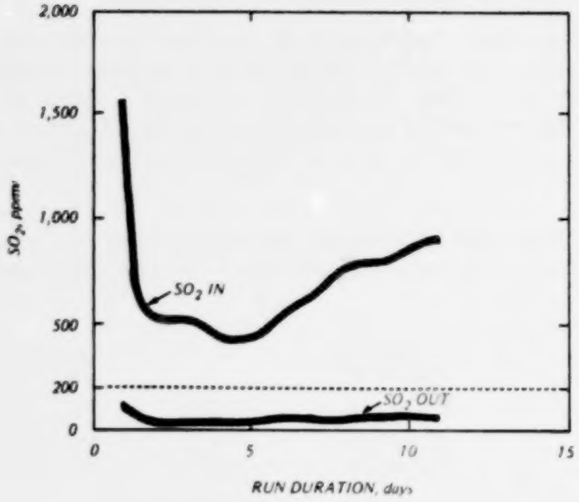
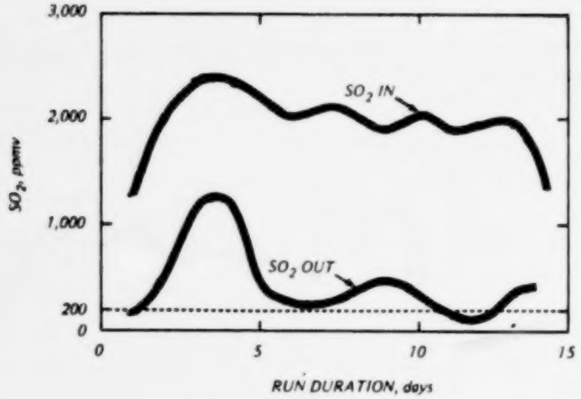


Figure 2. Inlet and outlet $SO_2$ concentrations during run no. 2.



*THE POOR $SO_2$ RECOVERIES DURING THIS PERIOD RESULTED FROM POOR QUALITY SOLUTION CAUSED BY MECHANICAL PROBLEMS IN THE SODA ASH FEED SYSTEM AND EVAPORATION AREA, AND LOW FEED RATES TO THE ABSORBER WHILE BALANCING TANK INVENTORIES.*

Figure 3. Inlet and outlet $SO_2$ concentrations during run no. 3.

Following the start of preheat on July 23, 1976, the $SO_2$ reduction section of the FGD plant was operated on $SO_2$ process gas for the first time on November 17, 1976. $SO_2$ feed rate was about 14,000 scfh (392 $m^3/h$) or 55 percent of rated capacity. Difficulty was encountered in properly draining the condensed sulfur from the sulfur condensers to the sulfur pit, and the reduction section was put back on hot standby on November 18, 1976.

Modifications were made to the reduction system and the system was ready to resume operation on $SO_2$ on November 28, 1976, when the main steam supply from Unit No. 11 to the FGD plant was shut down for replacement of an attemperator water line gasket. During this shutdown, the emergency steam supply system failed to operate properly and major freezeup problems occurred in the outdoor areas of the FGD plant. During December 1976, repairs were completed, and Unit No. 11 was shut down during the first 2 weeks of January 1977 for scheduled boiler maintenance.

On January 15, 1977, during startup of the Unit No. 11 boiler, a major mishap resulted in an extended outage of the boiler. The mishap was in no way connected with or caused by FGD plant operation.

Repairs to the Unit No. 11 boiler were started immediately and during this period various work was performed throughout the FGD plant in preparation for integrated operation scheduled for May 15, 1977. The Unit No. 11 boiler was actually restarted for the first time on May 5, 1977, but was limited to half load until July 11, 1977, because of problems with the west air preheater.

The booster fan and absorber were started up on May 27, 1977, with Unit No. 11 operating at about 50 to 60 MW gross. The $SO_2$ reduction system was started on June 14, 1977, and operated until June 16, 1977. Shutdown on June 16 resulted from lack of $SO_2$ feed gas due to a switch from high sulfur to low sulfur coal on Unit No. 11. The reduction system was restarted on June 18, 1977, and operated through June 23, 1977, with the exception of June 20 when a shutdown was scheduled to install an additional sulfur drain line. An average of 13 tons (11.8 metric tons) per day of sulfur was produced from June 18 to June 22, 1977. The reduction system was shut down on June 24, 1977, for checkout of natural gas leakage through the switch valves for the primary reactor system and for modifications to the natural gas feed piping to eliminate any chance of leakage through the switch valves. This natural gas leakage had been coloring the sulfur product from the first sulfur condenser. The entire FGD plant remained down for the balance of June 1977.

Startup of the FGD unit began again on July 15, 1977, and various problems with the system and with Unit No. 11 were corrected prior to the start of the FGD plant acceptance test on August 29, 1977.

## Acceptance Test Performance

The Wellman-Lord/Allied Chemical FGD plant was contractually bound to meet specific performance criteria before the plant could be "accepted" by NIPSCO from Davy Powergas and before the year-long continuous test program could begin. The acceptance test performance criteria follow:

## Performance Criteria

1. The Contractor (NIPSCO) guarantees that during the acceptance testing the system will perform on Unit No. 11 as follows:

   (a) The system, when operated with nominal 3% sulfur in the coal, shall achieve 90 percent sulfur dioxide removal from the flue gas entering the absorber.

   (b) The system's particulate emission rate shall not exceed the Federal New Source Performance Standard for Fossil-Fuel Fired Steam Generators that is current at the completion of Phase I.

   (c) Based on the following costs, the net operating cost per hour shall not exceed $56.00.

| | |
|---|---|
| Electric Power | $0.007/kWh |
| Steam | $0.50/1,000 lb (373 kg) at 550 psig<br>(31.8 kg/cm$^2$) and 750° F (399° C) |
| Natural Gas | $0.55/1 million Btu |

   (d) The average chemical makeup over a 12-day operating period at an average of 320,000 acfm (8,960 m$^3$/min) (92 MW equivalent) shall be no greater than 6.6 tons (6 metric tons) of $Na_2CO_3$ per day. The value of antioxidant used during the 12-day period shall not exceed an average of $400 per day.

   (e) The system shall be capable of producing byproduct sulfur having a sulfur assay of 99.5 percent minimum and shall be suitable for use in a sulfur-burning sulfuric acid plant.

2. The Performance Criteria in paragraphs (a) through (e) above shall be demonstrated in accordance with the following paragraphs which cite the provisions by which the unit will be operated during the acceptance test:

   NIPSCO shall hold Davy Powergas responsible for the successful completion of the acceptance test period; accordingly, Davy Powergas shall be required to maintain a technical staff available until such time as the performance criteria have been fulfilled in an acceptance test as follows:

   The test period shall consist of a 12-day test at an average load of 320,000 acfm (8,960 m$^3$/min) (92 MW equivalent) followed by an 83-hour test at an average load of 390,000 acfm (10,920 m$^3$/min) (110 MW equivalent). During the test period the sulfur content of the coal will be nominal 3% sulfur. Interruptions totalling less than 24 hours will not be considered as a break in continuous operation except that the test period will be extended by this period of interruption. Furthermore, if, for reasons beyond the Contractor's control, there is either a reason to separate the 92-MW and 110-MW test runs, having completed no less than 10 days of the 12-day test, or else the 110-MW test portion of the test has not been completed, then the 110-MW test can be restarted preceded by 3 days at 92 MW operation.

Should, for reasons beyond the Contractor's control, it become necessary to adjust the basis for the performance criteria run, then Davy Powergas will prepare new performance procedures consistent with the performance criteria in this contract. In no event will the emission criteria be changed.

As indicated in the acceptance test performance criteria statement above, the acceptance test period was divided into two phases:

Acceptance Test Phase I --12-day test at an average flue gas flow rate of 320,000 acfm (8,960 $m^3$/min) (92 MW equivalent).

Acceptance Test Phase II--83-hour test at an average flue gas flow rate of 390,000 acfm (10,920 $m^3$/min) (110 MW equivalent).

Details on the actual performance of the system during the test periods and comparisons to the performance criteria are presented below.

## Acceptance Test Phase I

During acceptance test Phase I, the FGD plant was required to meet the performance criteria indicated above while the boiler was firing a nominal 3% sulfur coal and producing an average of 320,000 cfm (8,960 $m^3$/min) of flue gas at 300° F (149° C). Each performance criterion is reviewed below and compared to actual results obtained during the 12-day acceptance test period.

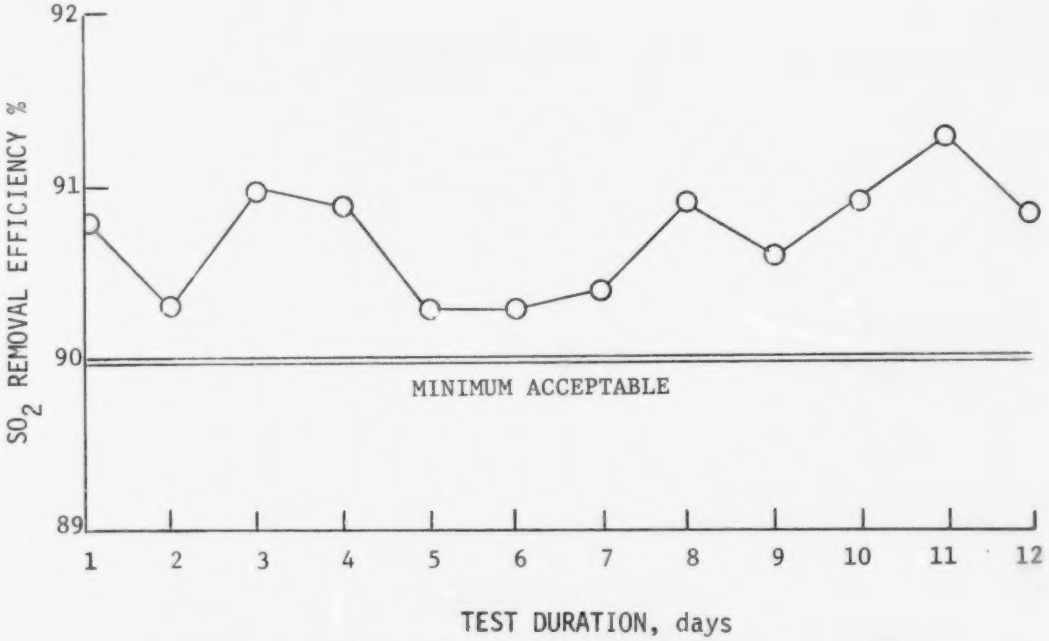


Figure 4. $SO_2$ removal efficiencies during 12-day test.

SO$_2$ Removal Efficiency--The FGD plant was required to remove 90 percent or more of the SO$_2$ in the boiler No. 11 flue gas. The data taken from continuous monitoring equipment and averaged over each 2-hour period are presented in figure 4. Figure 4 shows that the actual performance of the plant exceeded the SO$_2$ removal performance criterion during the entire test period.

Particle Emissions--Particle emissions from the FGD plant stack were to be limited to the Federal New Source Performance Standard (NSPS) for coal-fired boilers in effect at the completion of the design phase of the project. That standard was (and remains) 0.1 lb (0.04 kg) of particle emissions per 1 million Btu of heat input to the boiler. Figure 5 shows the NSPS particle emission limitation and the actual performance of the FGD plant in removing particulate matter. The data presented are based on the average of a 3-hour particle sample taken on the days specified. As figure 5 indicates, the FGD plant consistently operated within the established particle emission limitation.

Operating Cost for Electricity, Steam, and Natural Gas--Based on the following predetermined costs for electricity, steam, and natural gas, the operating cost of the FGD plant was required to be $56/hour or less for successful acceptance test operation:

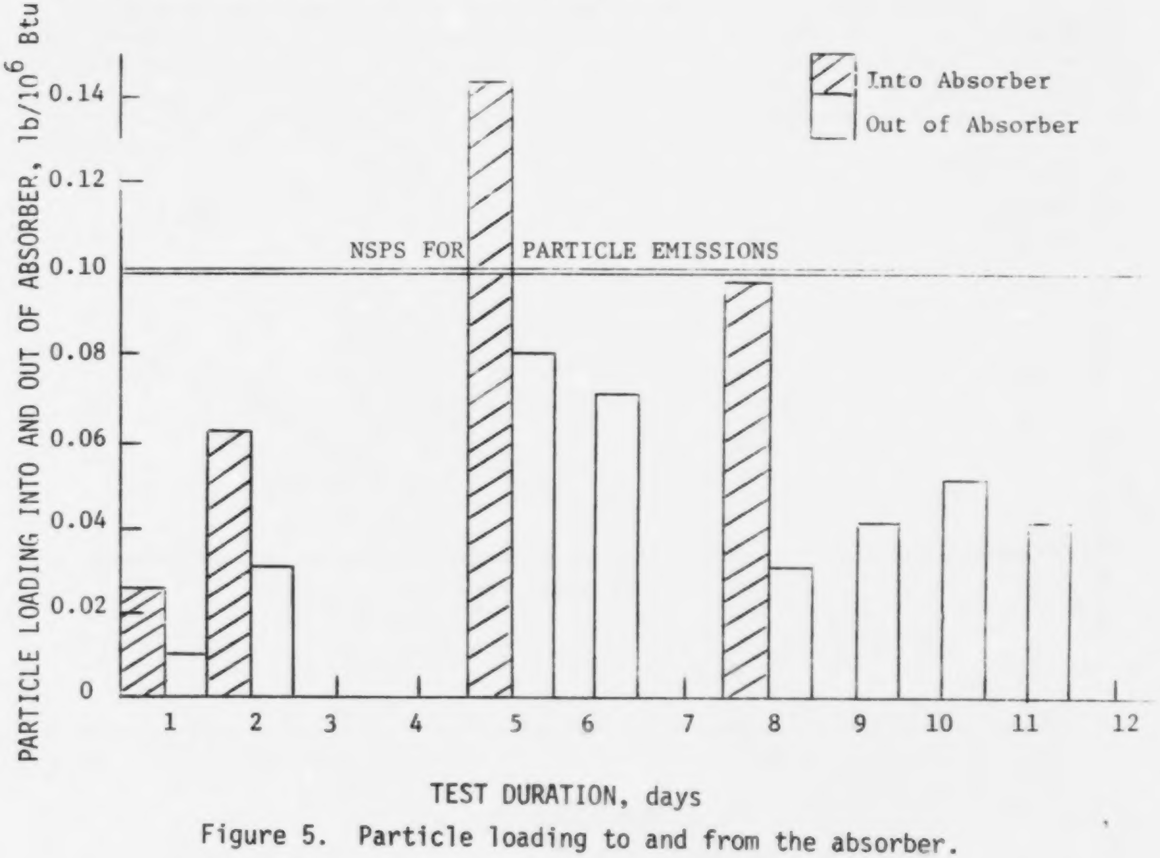


Figure 5. Particle loading to and from the absorber.

| | |
|---|---|
| Electricity: | \$0.007/kWh |
| Steam: | \$0.05/1000 lb (373 kg) at 550 psig ($31.8\ kg/cm^2$) and 750° F (399° C) |
| Natural Gas: | \$0.55/1 million Btu |

Sodium Carbonate ($Na_2CO_3$) Makeup--During the absorption process, some of the sodium sulfite ($Na_2SO_3$) in the scrubbing solution is converted to sodium sulfate ($Na_2SO_4$). Since the $Na_2SO_4$ will not react with $SO_2$, it must be purged from the system to maintain the scrubbing solution quality at the proper level for maximum $SO_2$ removal efficiency. Some additional sodium compounds are removed from the system with the residue on the flyash filter between the absorber surge tank and the evaporator. The sodium removed from the system by these mechanisms must be made up by the addition of $Na_2CO_3$. The rate of $Na_2CO_3$ addition, averaged over the 12-day test period, was limited to 6.6 tons/day (6 metric tons/day).

Sulfur Product Purity--Under the operating conditions specified for the acceptance test period, the FGD plant produces approximately 25 tons (22.7 metric tons) of molten sulfur per day. The performance criterion for purity of the byproduct sulfur required that a 12-day composite sample contain less than 0.5 percent impurities.

From the summary comments above, it is apparent that the FGD plant successfully met all of the required performance criteria during the 12-day test period. The performance criteria and actual performance data are summarized in table 1 below for easy comparison.

TABLE 1

SUMMARY OF FGD PLANT PERFORMANCE CRITERIA AND ACTUAL PERFORMANCE DATA FROM THE 12-DAY ACCEPTANCE TEST PERIOD

| Variable assessed | Performance criteria | Actual performance (average) |
|---|---|---|
| $SO_2$ removal efficiency, % | 90 | 91 |
| Particle emissions, $lb/10^6$ Btu ($kg/10^6$ Btu) | 0.1 (0.04) | 0.04 (0.01) |
| Steam, electricity, gas cost \$/h | 56 | 43 |
| Sodium carbonate makeup, tons/day (metric tons/day) | 6.6 (6) | 6.2 (5.6) |
| Sulfur product purity, % | 99.5 | 99.9 |

During the 83-hour test period, the FGD plant was required to meet $SO_2$ and particle emissions criteria while the boiler was operating at a flue gas flow rate of 390,000 acfm (10,920 $m^3$/min) (110 MW equivalent). Under these stringent operating conditions, the $SO_2$ removal efficiency averaged 91 percent. The average $SO_2$ emission rate was 0.5 lb/1 million Btu (0.19 kg/1 million Btu), 42 percent of the NSPS for $SO_2$ emissions. Particle emissions averaged 0.03 lb/1 million Btu (0.11 kg/1 million Btu), 30 percent of the NSPS for particle emissions.

## Maximum Capacity Test

During the acceptance test period, it was evident that flue gas rates from the boiler for a given energy production rate had increased significantly since the boiler baseline test was conducted in 1974 and 1975. Because of the increase in boiler flue gas rates, there was concern that the FGD plant--designed on the basis of 5-year-old boiler data--might not be able to process the flue gas from the boiler at maximum load under current operating conditions. Therefore, at the conclusion of the 83-hour high-load test at a flue gas flow rate of approximately 390,000 acfm (10,920 $m^3$/min) (110 MW equivalent), the boiler output was gradually increased, with the FGD plant booster fan speed correspondingly increased to take the full flow of the flue gas from the boiler. At a flue gas flow rate of 460,000 acfm (12,880 $m^3$/min) (118 MW equivalent), the two induced draft fans on the boiler outlet reached their maximum speed. At this peak boiler load, the FGD plant booster fan had approximately 10 percent remaining capacity, indicating that the FGD plant could process flue gas flow rates of approximately 506,000 acfm (14,168 $m^3$/min) (130 MW equivalent) for brief periods, if necessary.

## Problems Encountered

Problems encountered during the acceptance test period are categorized according to their occurrence in (1) the boiler, (2) the $SO_2$ recovery process, or (3) the $SO_2$ reduction process.

Boiler Problems--During the 12-day test period, 19 of a total of 31 hours of interruption were attributable to the boiler. Ten hours of interruption were the result of the intermittent tripping of a pressure sensitive switch in the duct upstream of the FGD plant booster fan which resulted in several unexpected interruptions of the booster fan operation. The problem was corrected when it was discovered that water had caused an electrical short in the switch. The remaining 9 hours of interruption attributable to the boiler were the result of a boiler feedwater pump failure and subsequent repairs. Since these interruptions totalled only 19 hours out of the total 288 hours (12 days) scheduled for the acceptance test and since the interruptions were wholly attributable to boiler-side problems, no penalty was assessed to the FGD plant as a result of these interruptions.

$SO_2$ Recovery Process Problems--$SO_2$ removal efficiencies in the $SO_2$ recovery process were 89 percent (rather than the required 90 percent) during two 2-hour averages. The acceptance test period was extended by 4 hours to a total of 292 hours, and no further violations of acceptance test performance criteria occurred.

$SO_2$ Reduction Process Problems--The pressure drop across the Claus reactor in the $SO_2$ reduction area increased beyond design values, requiring an 8-hour shutdown for correction of a sulfur collection problem in the reactor. While such an occurrence is defined as an "interruption" by the acceptance test performance criteria, the FGD plant was not penalized for the interruption because in normal, nontest operation, the problem could have been corrected while the $SO_2$ recovery process continued to operate with spent liquor from the absorber being stored in the plant's surge tank until the $SO_2$ reduction process was fully functional again.

83-Hour Test Period--During the 83-hour test period, 3 hours of "interruption" occurred. One hour was attributable to a turbine vacuum problem which resulted in the boiler output being reduced to 55 MW instead of the test requirement of 110 MW. The remaining 2 hours were attributable to a 2-hour average $SO_2$ removal efficiency reading of 89 percent rather than the required 90 percent. All 3 hours of "interruption" time were added to the end of the 83-hour test period.

### Acceptance Test Conclusions

Continuous comparison of actual performance data from the FGD plant to performance criteria established in the NIPSCO/EPA contract verified the outstanding performance of the plant during the acceptance test period. On September 15, 1977, 14 hours after the conclusion of the acceptance test period, EPA officially notified NIPSCO that the performance requirements specified in the NIPSCO/EPA contract had been successfully fulfilled. NIPSCO similarly informed Davy Powergas of the utility's acceptance of the system on September 16, 1977. At the conclusion of the acceptance test period, the demonstration test year began.

## Postacceptance Test Operation

The EPA/NIPSCO contract specifies that the FGD unit will be operated for 1 year after satisfactory completion of the acceptance test. This demonstration test year began on September 16, 1977.

During this 1-year demonstration test, data will be collected to characterize the operation of the Unit No. 11 and the FGD plant.

Information collected during the demonstration test year will include data relating to:

1. Unit No. 11 fuel and its utilization.
2. Power production.
3. Flue gas quantity and quality.
4. FGD plant utility requirements and their costs.
5. Makeup chemical requirements.

6. Maintenance requirements, nature, and costs.

7. Operating requirements and costs.

8. Reliability of the FGD system.

9. Byproduct sulfur quantity, quality, and price obtained.

10. Quantity and quality of, and the price obtained for, the purged sodium sulfate granular solids.

11. Other information that would be useful for characterizing the operating performance and cost of the $SO_2$ recovery/reduction to sulfur system.

During the year-long test period, the Environmental Engineering Division of TRW, Inc., under contract to the EPA, will conduct a series of tests of system emissions, fuel and ash analyses, boiler efficiencies, and other system characteristics. During this time, tests will also be performed with Unit No. 11 using coals with sulfur contents that are significantly higher and lower than the normal 3.15% to 3.5% sulfur. The results of these demonstration year tests will be compared to the results of the baseline test which was performed on Unit No. 11 by TRW, Inc., prior to installation of the FGD plant.

The normal operating and maintenance staff of the FGD plant consists of:

3 administrators,
4 supervisors,
14 operators,
8 mechanics, and
2 analysts.

Operators are scheduled three men per 8-hour shift, 7 days per week. Administrators, supervisors, mechanics and analysts normally are scheduled for 8 hours per day, 5 days per week.

The nine Unit No. 11 operators (three per shift) in the generating station spend approximately a total combined time of 3 hours per day on FGD plant related activities.

It is premature at this time to comment on demonstration test year results. However, we can state that as of October 20, 1977, the FGD plant has recovered 699 long tons (710 metric tons) of marketable quality elemental sulfur.

## Future Plans for the FGD Plant

Of primary concern during the 1-year demonstration test period will be the collection and evaluation of performance and economic data. TRW will prepare a final report which will present the data collected over the 1-year period. It is planned that the FGD plant will follow normal Unit No. 11 boiler operation (boiler startup, shutdown, load changes, fuel changes, etc.) during the demonstration test year.

## Comparison with Alternate Emission Controls

NIPSCO will also be comparing the Wellman-Lord/Allied FGD system operating and economic characteristics with $SO_2$ emission control alternatives. The other three generating units at Dean H. Mitchell Station are presently burning low sulfur Western coal, which presents an opportunity for comparing the low sulfur coal alternative with the Wellman-Lord/Allied Chemical FGD system.

## Alternate Gaseous Reductant Studies

In 1972 when the NIPSCO FGD plant was designed, there was little or no concern that the process required the use of approximately 14,000 scf of natural gas per long ton (386 $m^3$/metric ton) of sulfur produced. However, the cost and (particularly) the availability of natural gas have changed drastically in the 5 years since the system was designed, and the use of an alternate reductant is needed to alleviate this unanticipated disadvantage of the system. EPA and NIPSCO are considering joint investigation of alternate gaseous reductants including gases generated by the gasification of coal. It is visualized that hydrogen and carbon monoxide sources such as low Btu gas would be suitable for the $SO_2$ reduction installation at NIPSCO. If a suitable technology is identified that shows economic and technical promise for demonstration with the Wellman-Lord/Allied Chemical FGD plant at NIPSCO, the currently scheduled year-long test period may be extended to include the demonstration of alternate gaseous sources for the reduction of $SO_2$ to sulfur in the Allied reduction installation.

## $SO_2$ Coal Conversion

The ultimate reductant source is the abundant supply of coal. Allied Chemical has developed technology for the direct reduction of $SO_2$ to sulfur utilizing a wide range of steam coals. A longer range demonstration program to advance this technology to commercial availability is also under consideration for the NIPSCO FGD site.

## High Efficiency Absorber Operation

EPA has indicated an interest in extending the demonstration period beyond 1 year to assess the effect of the addition of a fourth Koch valve tray to the absorber on $SO_2$ removal efficiency. Preliminary studies suggest that a fourth tray would permit $SO_2$ removal efficiencies in excess of 95 percent. Removal efficiencies in this range could allow attainment of NSPS for $SO_2$ (1.2 lb/1 million Btu or 0.45 kg/1 million Btu) while bypassing some untreated flue gas to reheat the treated flue gas. In addition, the demonstration of high efficiency absorption capability would be pertinent in case the Federal NSPS for $SO_2$ were to be made more stringent. A second area of interest in the study of high efficiency absorber operation is the evaluation of a novel tray design in place of the conventional Koch tray. The novel tray design developed by Merix Corporation may be installed as the fourth tray in the absorber to evaluate the tray's $SO_2$ removal capabilities and to demonstrate in field application that the tray can operate effectively and efficiently without recirculating scrubbing solution to the tray. The developer claims that the makeup sodium carbonate solution alone will provide sufficient flow to support satisfactory operation of the tray.

## Energy/Economic Optimization

The first year of demonstration testing will determine the ability of the FGD plant to follow the typical operating requirements imposed by the boiler during the year. The test and evaluation program is important and significant from the standpoint of demonstrating the plant's versatility, reliability, and operability. Operating cost data will also be logged for comparison to the costs of other $SO_2$ control alternatives. An extension of the test period would permit optimization of the energy and economic demands of the plant to the benefit of NIPSCO and other potential users who may use the same or similar technology in the future.

## Comparative Assessment of Oil- Versus Coal-Fired Boilers

EPA's Industrial Environmental Research Laboratory at Research Triangle Park has initiated a program for the comprehensive environmental assessment of conventional combustion processes. One aspect of that program is the comparative assessment of a well-controlled utility boiler firing coal and a well-controlled utility boiler firing oil. NIPSCO's boiler No. 11 is being considered for investigation as the well-controlled coal-fired boiler in this study. At the sites chosen, EPA will conduct comprehensive characterizations of all inlet streams to and outlet streams from the boiler and its control equipment. The feedstream and emissions characterization data will be used to assess the environmental, economic, social, and energy impacts of the combustion system and associated pollution control equipment.

We expect that the data obtained over the 1-year demonstration period and from any additional testing will be definitive and will be of value to the utility industry in relation to the decisions yet to be made about $SO_2$ emission controls.

# DESIGN OF THE 100 MW ATOMICS INTERNATIONAL AQUEOUS CARBONATE PROCESS REGENERATIVE FGD DEMONSTRATION PLANT

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## ABSTRACT

A program is now underway to design, build, test, and operate a 100 MW second generation flue gas desulfurization (FGD) demonstration plant for the New York State electric utilities. The program is jointly sponsored by the Empire State Electric Energy Research Corporation and the U.S. Environmental Protection Agency. The FGD process to be demonstrated is the Atomics International (AI) Aqueous Carbonate Process (ACP).

Phase I of the program started on January 3, 1977, and was completed on May 20, 1977. The results are a preliminary design of the demonstration plant, a final estimate of the cost for completing the demonstration plant program (final design, procurement, construction, startup, and operation for one year), cost projections for 500 MW and 1000 MW ACP plants, and a work plan for Phase II.

This paper briefly describes the ACP process and also describes the demonstration plant which will be built and operated by AI at the Huntley Generating Station of the Niagara Mohawk Power Corporation.

# I. INTRODUCTION

A program is now underway to design, build, test, and operate a 100 MW second generation flue gas desulfurization (FGD) demonstration plant for the New York State electric utilities. The program is sponsored by the Empire State Electric Energy Research Corporation (ESEERCO)* and the U.S. Environmental Protection Agency (EPA); the FGD process to be demonstrated is the Atomics International (AI) Aqueous Carbonate Process (ACP). Phase I of the program started on January 3, 1977, and was completed on May 20, 1977. This paper briefly describes the ACP and then describes the results of the Phase I preliminary design of the demonstration plant which will be built and operated by AI at the Huntley Generating Station of the Niagara Mohawk Power Corporation.

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*Note: ESEERCO is a non-profit research and development corporation. Its members are Central Hudson Gas & Electric Corporation; Consolidated Edison Co. of N.Y. Inc.; Long Island Lighting Company; New York State Electric & Gas Corporation; Niagara Mohawk Power Corporation; Orange and Rockland Utilities, Inc.; Power Authority of the State of New York; and Rochester Gas and Electric Corporation.

## II. THE AQUEOUS CARBONATE PROCESS

The ACP is an advanced, regenerative, sodium carbonate-based FGD process which uses a spray dryer as a scrubber, solid carbon as the sulfur oxide reducing agent, and produces elemental sulfur as the byproduct. There are six major process steps in the ACP. These are (1) flue gas scrubbing, (2) spent absorbent collecting, (3) reduction, (4) quenching and filtration, (5) carbonation, and (6) sulfur production. Figure 1 is a block flow diagram which shows these process steps as they would be assembled for application to an existing power plant.

The scrubbing and spent absorbent collecting steps are coupled to the power plant, and to each other, by the flue gas stream which flows through them. They make up the gas-cleaning subsystem. The remaining four process steps are decoupled from the gas-cleaning subsystem by providing adequate storage capacity for both spent absorbent and regenerated scrubbing solution; they make up the regeneration subsystem. The decoupled feature of the process is emphasized by the dashed line in Figure 1, which separates the gas cleaning and regeneration subsystems.

# ACP BLOCK FLOW DIAGRAM

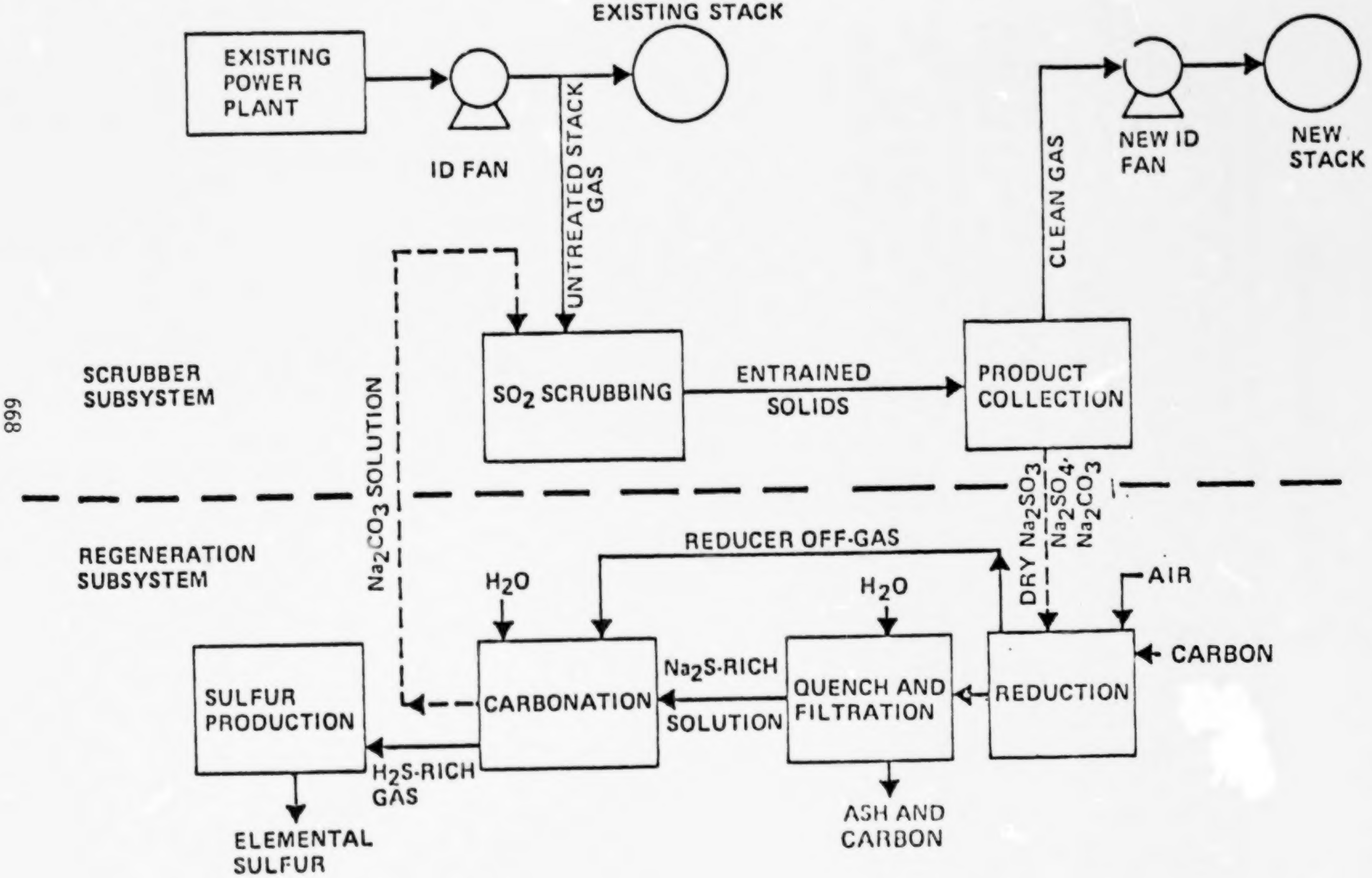


Figure 1

# III. THE FGD DEMONSTRATION PLANT

## A. THE DEMONSTRATION PLANT PROGRAM

The ACP demonstration plant program is being sponsored jointly by the Empire State Electric Energy Research Corporation (ESEERCO) and the U.S. Environmental Protection Agency (EPA).

## B. PROGRAM SCHEDULE

The program resulted from an ESEERCO response to the EPA Request for Proposal DU-75-A175 for programs to demonstrate advanced regenerable flue gas desulfurization processes; a four-phase program is called for with the following scope and schedule:

| | | |
|---|---|---|
| Phase I | Preliminary Design and Final Cost Estimate | January 3 - May 20, 1977 |
| Phase IA | Review of Phase I | May 20 - August 1977 |
| Phase II | Plant Supply (Final Design, Procurement, Construction) | August 1977 - September 1979 |
| Phase III | Acceptance Test | October - December 1979 |
| Phase IV | Test Operations | December 1979 - December 1980 |

Phase I started on January 3, 1977, and was completed on schedule 20 weeks later on May 20, 1977. The principal results of Phase I are a complete preliminary design of the demonstration plant and a final cost estimate for Phases II, III, and IV of the program. Cost projections for 500 MW and 1000 MW plants were also generated. The results of Phase I are currently being reviewed by ESEERCO and the EPA.

Although the start of Phase II has been delayed from the schedule projected during Phase I, the relative relationships of the remaining tasks are unchanged, and the length of the tasks will remain approximately the same except where there is an effect of winter weather at the construction site.

## C. PROGRAM COST ESTIMATE

The preliminary design work of Phase I was done over a period of 20 weeks at a program cost of $300,000 and is very detailed and thorough. Because of this, the cost estimate based on the design work is believed to be quite accurate.

The cost of Phase II, the plant supply phase, is estimated at \$18,124,270, startup (Phase III) is estimated at \$883,802, and the one-year test program is estimated to cost \$3,352,907 for a total program cost of \$22,370,979. In addition, it is recommended that \$1,671,500 be kept as a general program reserve. All of these costs are escalated according to the program schedule shown in Figure 2.

## D. DEMONSTRATION PLANT PROCESS

### 1. Design Basis

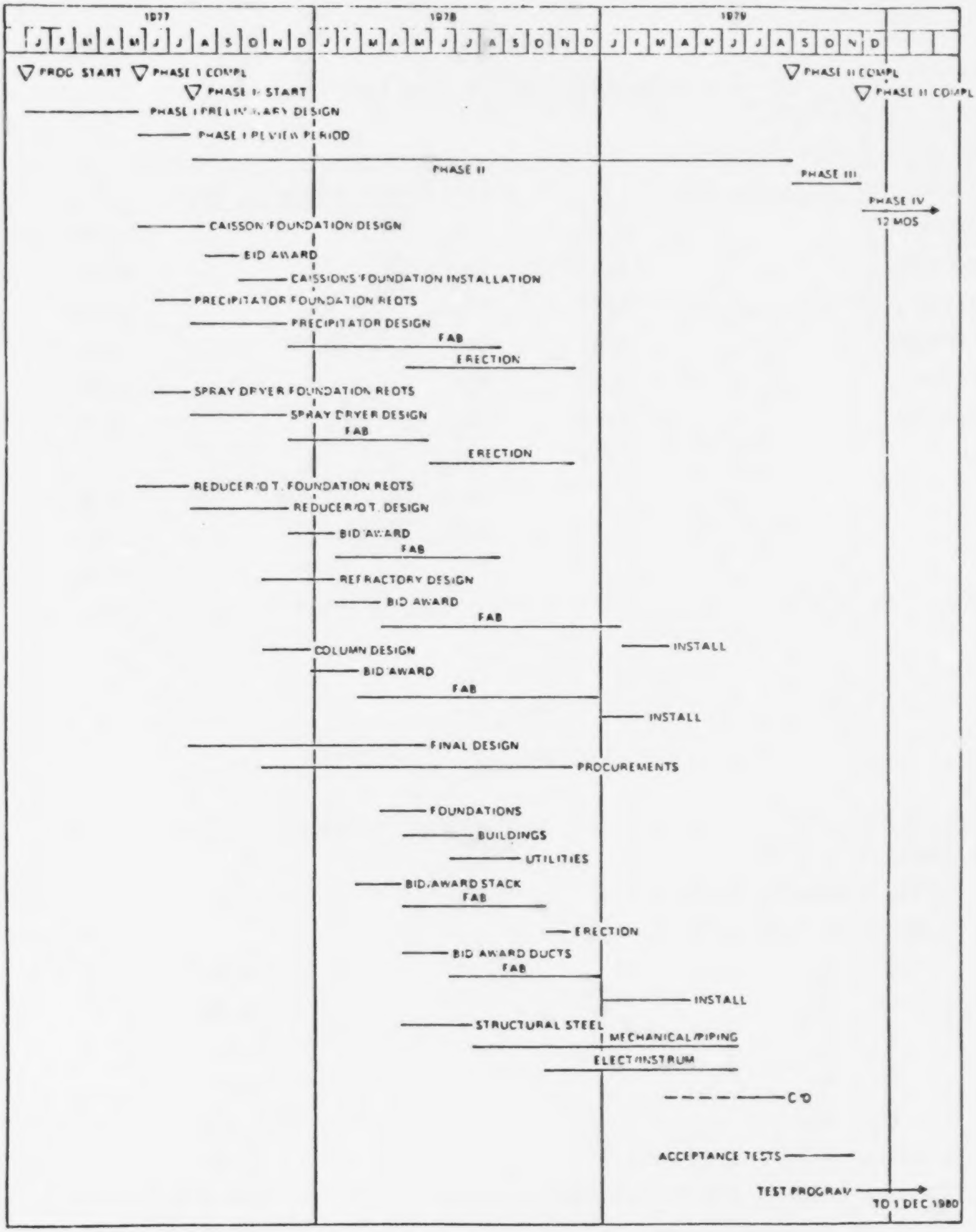
The Demonstration Plant is designed to treat the full 300,000 scfm flue gas stream generated by Unit 66 of the C. R. Huntley Station when operating at the 100 MW level, and to regenerate spent absorbent at a rate equivalent to an average power level of 60 MW.

The fuel for Unit 66 will be a Williams coal containing a nominal 2.5% sulfur. The coal composition is given in Table I. When this coal is burned, the flue gases will have the characteristics listed in Table II. The gas cleaning subsystem is designed to remove at least 90% of the $SO_2$ from this flue gas and to discharge the cleaned flue gas at a temperature at least 50°F above its water dewpoint and containing less than 0.01 gr/scf of particulate matter.

The regeneration subsystem is designed to run as a steady-state, base-loaded chemical plant. Its design throughput is equal to the spent absorbent production rate of the gas cleaning subsystem when the flue gas flow is at the 60 MW rate. A two-day surge capacity for spent absorbent and scrubbing solution is incorporated in this design. The regeneration subsystem is designed to use petroleum coke as the reducing agent, but the capability to perform tests with coal has been designed in.

### 2. Gas Cleaning Subsystem

Flue gas enters the spray dryer scrubber at a flow rate of 299,800 scfm, a temperature of 320°F, and with an $SO_2$ concentration of 1365 ppm (wet). The tail gas from the Claus plant is recycled to the scrubber at a flow rate of 5162 scfm, a temperature of 500°F, and with an $SO_2$ concentration of 1823 ppm. This gas stream is mixed with the boiler flue gas to produce a net gas flow rate of 304,977 scfm, at a temperature of 325°F, and with an $SO_2$ concentration of 1374 ppm. The flue gas flows downward through a finely atomized spray of scrubbing solution in the spray dryer. The scrubbing solution, at a flow rate of ~65 gpm and an effective sodium carbonate concentration of 22.3 wt %, is diluted with 43 gpm of process water before contacting the flue gas in the dryer. The sodium carbonate reacts with and neutralizes approximately 92.7% of the $SO_2$; the heat from the flue gas evaporates the water from the droplets, forming dry particles made up of a mixture of sodium sulfite, sodium



Schedule Bar Chart

Figure 2

## TABLE I

## COMPOSITION OF WILLIAMS COAL

| Ultimate Coal Analysis, Dry | % | Ultimate Ash Analysis, Dry | % |
|---|---|---|---|
| Carbon | 78.05 | $SiO_2$ | 38.80 |
| Hydrogen | 5.36 | $Fe_2O_3$ | 22.17 |
| Oxygen | 5.54 | $Al_2O_3$ | 21.21 |
| Nitrogen | 1.45 | CaO | 5.96 |
| Sulfur | 2.50 | MgO | 1.24 |
| Chlorine | 0.07 | $SO_3$ | 6.19 |
| Ash | 7.03 | $P_2O_5$ | - |
| | | $Na_2O$ | 1.28 |
| | | $K_2O$ | 1.21 |
| | | $TiO_2$ | 0.96 |

## TABLE II

## DESIGN FLUE GAS CHARACTERISTICS

| | |
|---|---|
| Temperature (°F) | 320 |
| Particle Loading (gr/scf) | 0.05 |
| Composition (vol %, dry basis) | |
| a) $N_2$ | 79.50 |
| b) $CO_2$ | 10.88 |
| c) $O_2$ | 8.51 |
| d) Ar | 0.97 |
| e) $SO_2$ | 0.143 |
| Molecular Weight of Dry Gas | 30.24 |
| Moisture Content (vol %, wet basis) | 5.0 to 6.5 |
| Full-Load Flow (scfm, wet, 70°F, 1 atm) | 300,000 |

sulfate, unreacted sodium carbonate, and agglomerated ash. Chlorides in the form of HCl acid mist also enter with the flue gas at a rate of about 60 lb of HCl gas (based on a coal firing rate of 83,300 lb/h of a coal containing 0.07 wt % chlorine). The scrubbing solution reacts with 97% of the HCl mist to form sodium chloride which is thus also present in the spent absorbent mixture.

The flue gas at a flow rate of 322,862 scfm, a temperature of 170°F, an $SO_2$ concentration of 95 ppm, and entrained spent absorbent at 4.27 gr/scf leaves the dryer and enters a two-stage particle collection system consisting of cyclones followed by an electrostatic precipitator. The two banks of eight cyclones remove approximately 11,271 lb/h of spent absorbent, and reduce the particle concentration to 0.2 gr/scf at the cyclone exit. The gases leave the cyclones and enter an electrostatic precipitator in which an additional 497 lb/h of spent absorbent is collected. The precipitator reduces the particle concentration to 0.01 gr/scf before discharge to the stack. The flue gas from the precipitator passes through an air-foil-type induced draft fan operating at 322,862 scfm, at 162°F, and 22-in. water suction pressure, and is exhausted into a 200-ft stack. The $SO_2$ concentration at the point of discharge from the plant is 95 ppm.

The spent absorbent is collected by a negative pressure pneumatic conveying system from the cyclones and precipitator and is transported to the storage hopper. The hopper provides a 48-h holdup of spent absorbent at the 100 MW level of operation. The spent absorbent is removed from the hopper with a variable speed weigh belt feeder and is transported pneumatically to the regeneration subsystem.

### 3. Regeneration Subsystem

#### a. Reducer

The spent absorbent and the carbonaceous material required for sulfate reduction (petroleum coke or coal) are removed from their respective storage hoppers through gravimetric weigh belt feeders and are conveyed pneumatically to the solids collection hopper at a rate of 7,077 lb/h of spent absorbent and 1,760 lb/h of carbon. The mixture of spent absorbent and carbon is removed from the hopper with a weigh belt feeder and is injected through three rotary air locks into the reducer vessel beneath the melt bed. This is done with a positive pressure conveying system through three conveying lines. The pneumatic conveying system uses approximately 1,662 lb/h (326 scfm) of recycled, cooled, and water-scrubbed reducer off-gas for conveying the solids into the reducer.

The reducer combustion air blower provides 9,436 lb/h (2,127 scfm) of air for the combustion of carbon in the reducer, in order to supply the heat necessary for preheating the incoming solids and air to 1800°F, and for making up the heat of reaction and vessel heat losses. The air from the blower, at a temperature of 265°F, passes through an indirect oil-fired air heater and is preheated to 1000°F. The air from the air heater is split into sixteen air nozzles and is injected into the reducer beneath the melt bed. The oil usage of the heater is 27 gal/h.

The flow rate of spent absorbent into the reducer is controlled by manually setting a ratio of spent absorbent to coke as a function of the $CO/CO_2$ ratio in the reducer off-gas. The flow rates of air and coke into the vessel are varied simultaneously by the melt bed temperature.

The sodium sulfite and sodium sulfate in the spent absorbent are reduced to sodium sulfide in a molten bed of sodium carbonate and sulfide at a nominal temperature of 1800°F. Approximately 4,856 lb/h of the molten mixture (smelt) of sodium carbonate, sodium sulfide, unreacted carbon, and ash are continuously withdrawn from the reducer through a spout located on one side of the vessel. In addition to the smelt, approximately 746 lb/h (148 scfm) of hot reducer off-gas flows from the reducer through the smelt spout.

The smelt is shattered, quenched, and dissolved (to form green liquor) in a cylindrical quench tank. The smelt is shattered by a 1000 lb/h steam jet, a low pressure green liquor recirculation nozzle (60 gal/min), and a low pressure quench tank water make-up nozzle (31 gal/min). The tank is equipped with an agitator to ensure adequate dissolution of the smelt. The quench tank temperature is maintained at approximately 220°F by the quench tank recirculation cooler.

The reducer off-gas, at a temperature of 1800°F, and containing 6 gr/scf of sodium chloride, sodium sulfate, and sodium carbonate particulate, flows from the reducer at 14,335 lb/h (2847 scfm) into the venturi scrubber where the gas is contacted with recycled solution sprays to remove particulate. The solution flow rate is 54,043 lb/h (108 gal/min) at a liquid/saturated gas ratio of about 20 gal/1000 $ft^3$. The reducer off-gas is saturated with water and is cooled to 140°F. The saturated gas, along with 47,200 lb/h (94 gal/min) of excess solution, flow from the venturi scrubber into the gas cooling tower.

Water is recirculated at 109,341 lb/h (219 gal/min) through the cooling tower to absorb heat from the reducer off-gas. Essentially all of the particles entrained in the off-gas (sodium chloride, sodium sulfate, and sodium carbonate) are removed from the off-gas in the venturi scrubber and the gas cooling tower and are purged from the system. The purge stream of 7,144 lb/h (14 gal/min) contains 0.75 wt % sodium chloride, 0.87 wt % sodium carbonate, and 0.40 wt % sodium sulfate.

The quench off-gas vapors, consisting of quench steam and reducer off-gas, are cooled and scrubbed in the quench off-gas tower cooler with a recirculating water stream. The bleed flow from the tower recirculation loop provides the make-up water for the quench tank.

### b. Filtration

The green liquor is pumped from the quench tank at a rate of 21,128 lb/h (35 gal/min) through the green liquor cooler where the temperature is reduced from 220°F to 100°F. The solids, consisting of unreacted ash and carbon, are concentrated in the liquid cyclone to an underflow solids concentration of about 5 wt %. The solids discharge from the cyclone flows into a rotary vacuum precoat ash filter in which the solids are removed from the green liquor, washed with fresh water, and discharged at 50% moisture from the system at a rate of 455 lb/h. The filtrate and wash water, at a rate of 4,098 lb/h (7 gal/min), are pumped along with the cyclone overflow (17,197 lb/h or 29 gal/min) into the green liquor storage tank. The tank provides 12 hours of liquor hold-up.

A green liquor surge tank has been provided to allow the ash filter to be taken off-line for precoating. The nominal thickness of precoat at the beginning of the cycle is 6 in., which is sufficient for 12 hours of continuous operation. During the period when the filter is off-line for re-precoating, the green liquor is stored in the surge tank. The time required to re-precoat the filter is 2 to 4 hours. As the filter is brought back on-line, it receives slurry from each of the liquid cyclones until the surge tank is emptied. The surge tank provides for 12 hours of liquor hold-up.

### c. Carbonation

The green liquor is contacted with the reducer off-gas in a series of sieve tray columns, producing a gas stream containing 31.9 vol % hydrogen sulfide (wet) and a liquid stream having an effective sodium carbonate concentration of 22.3 wt %. The process details are proprietary.

The regenerated carbonate flows from the carbonation system into a vertical tank, vertical leaf filter where a nominal 105 lb/h of wet cake is formed. At 50% moisture, the cake contains 23.3 lb/h of ash solids and 10 lb/h of precoat, with the remainder being process liquor; this is discharged on a batch basis.

After filtration, the liquor is stored in the scrubbing solution storage tank, which has a capacity sufficient for 48 hours of operation at the 100 MW level. Makeup sodium carbonate is periodically conveyed into the tank from a 20-ton self-unloading truck. The dry carbonate is contacted with a stream of recirculated scrubbing solution and fresh water and is dissolved. The tank is equipped with an agitator to aid in the dissolution of the carbonate. Based on the average steady-state carbonate makeup rate of about 200 lb/h, one truck will be required approximately every 8 days.

### d. Claus Plant

The Claus plant is a standard, commercial three-stage sulfur plant designed to recover 96.4% of the sulfur in the feed. The nominal recovery of sulfur from the feed stream is 13.53 ton/day.

### e. Plant Auxiliaries

The plant auxiliaries include the coal and coke unloading and storage system, ash disposal, cooling water, and process water.

Coke and coal are transferred from a delivery truck to their respective storage hoppers by a negative pressure conveying system using a common exhauster. The coke storage hopper has been sized for a 5-day capacity; the coal hopper has been sized for a 3-day capacity. The coal handling equipment excludes any coal drying and grinding equipment. It has been assumed that the coal would be removed from the Huntley Station coal pile and would be transported to a local facility where the necessary coal drying and grinding would be performed. The coal would then be returned by truck to the Huntley site and would be unloaded into the coal storage hopper.

The cooling water and process water requirements are supplied by vertical pumps located in the intake tunnel of Units 61 and 62. High pressure (60 psi) cooling and process water are supplied by centrifugal boost pumps. The cooling water is discharged back to the river through an existing 42-in. line.

The ash collection system receives wet ash cake from the ash filter and the leaf filter. The filters are located on the second floor of the filter building and the wet solids, at 50% moisture, flow by gravity into a sump located beneath the filters on the first floor. The ash solids are removed from the sump at a rate of 560 lb/h and are transported to the Huntley coal pile for final disposal.

## E. PLANT DESCRIPTION

### 1. Plant Location

The Demonstration Plant will be built within the boundaries of the C. R. Huntley Station of the Niagara Mohawk Power Corporation; the station is located in Tonawanda (near Buffalo), New York, on the east bank of the Niagara River. The location of the Demonstration Plant within the station boundaries is shown in Figure 3.

The Demonstration Plant will be located east of Unit 66, next to the existing electrostatic precipitators.

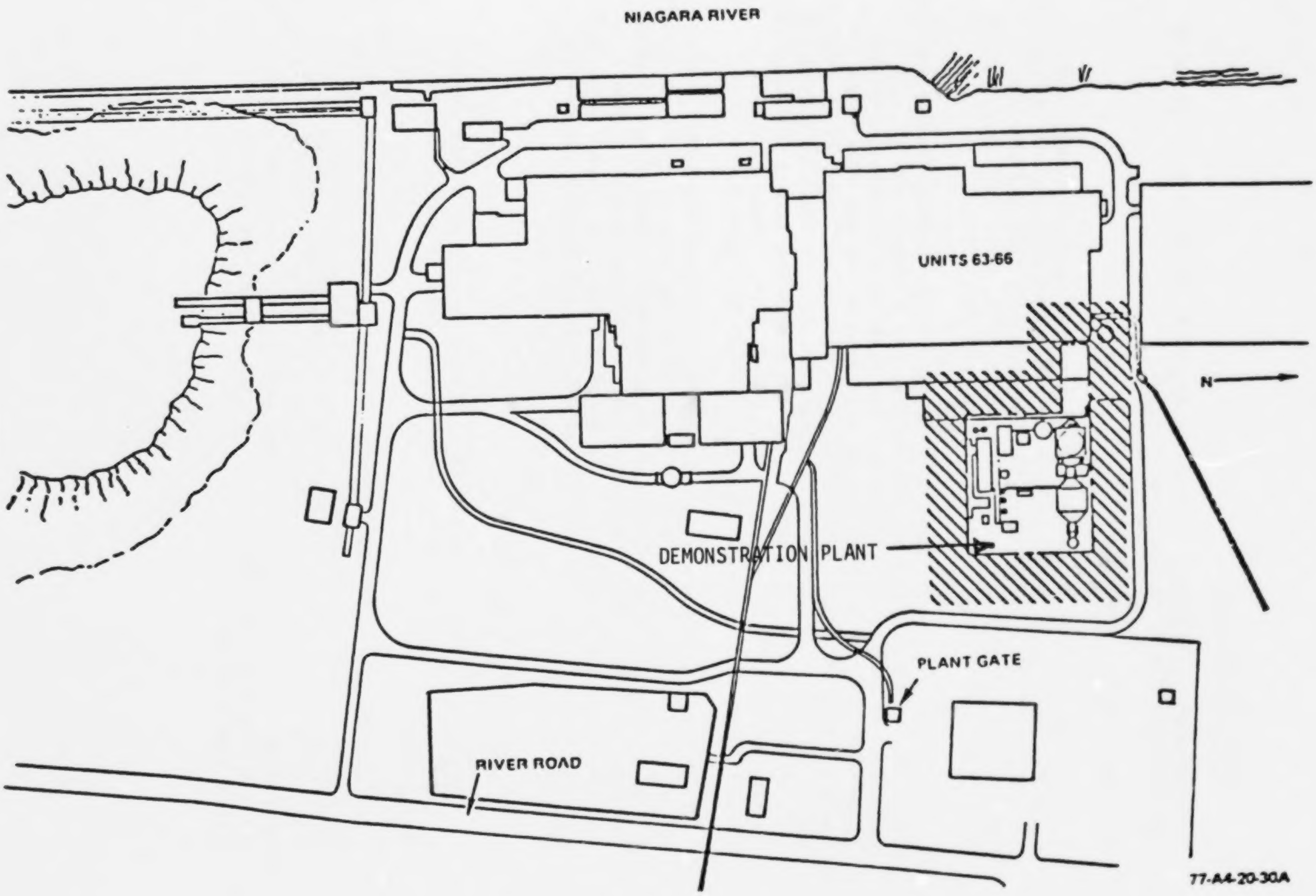


Figure 3. Location of ACP Demonstration Plant at Huntley Generating Station

## 2. Plant Description

The equipment arrangement is shown in Figure 4. A brief description of the Demonstration Plant equipment follows:

### a. Gas Cleaning Subsystem

The gas cleaning subsystem consists of the shut-off damper and ducting, the spray dryer scrubber, the spent absorbent cyclone collectors, the electrostatic precipitator, the induced-draft fan, and the new stack, plus the spent absorbent transfer system, spent absorbent storage hopper, scrubbing solution storage tank, and auxiliaries.

The spray dryer scrubber has a 42-ft diameter drying chamber containing 5 centrifugal atomizers. The chamber has a conical bottom, and is approximately 60 ft long. There are two banks of 8 cyclones, arranged in parallel so that one bank can be shut down at low gas flow rates. The electrostatic precipitator chamber is about 40-ft high, 45-ft wide, and 36-ft long. The ID fan is an air foil type with inlet vane control; it is driven by a 2250 hp motor. The fan discharges into a self-supporting carbon steel stack, 14-ft diameter by 200-ft high. These items of equipment make up the gas train and are shown in Figure 5.

The spent absorbent storage hopper is a vertical bin with a conical bottom, 26-ft in diameter, with a capacity of 248 tons of spent absorbent. The spent absorbent transfer system is a pneumatic system which conveys the spent absorbent from the cyclone and electrostatic precipitator hoppers to the storage hopper. The scrubbing solution storage tank is a vertical tank, 28-ft in diameter by 34-ft high and holding 158,600 gal of solution.

### b. Regeneration Subsystem

Reduction System: The reduction system is made up of the reducer, quench tank, reducer off-gas system, reducer preheat equipment, and auxiliaries.

The reducer is a 14-ft diameter OD steel vessel with conical top and bottom sections and rounded heads; it is about 32-ft tall. It is lined with a 15-in. layer of Monofrax A alumina blocks, backed by a 6-in. thick layer of Alfrax 66 castable refractory. It is supported by the reducer building structural steel and discharges reduced melt by gravity flow into the quench tank. Figure 6 shows the reducer and quench tank vessels.

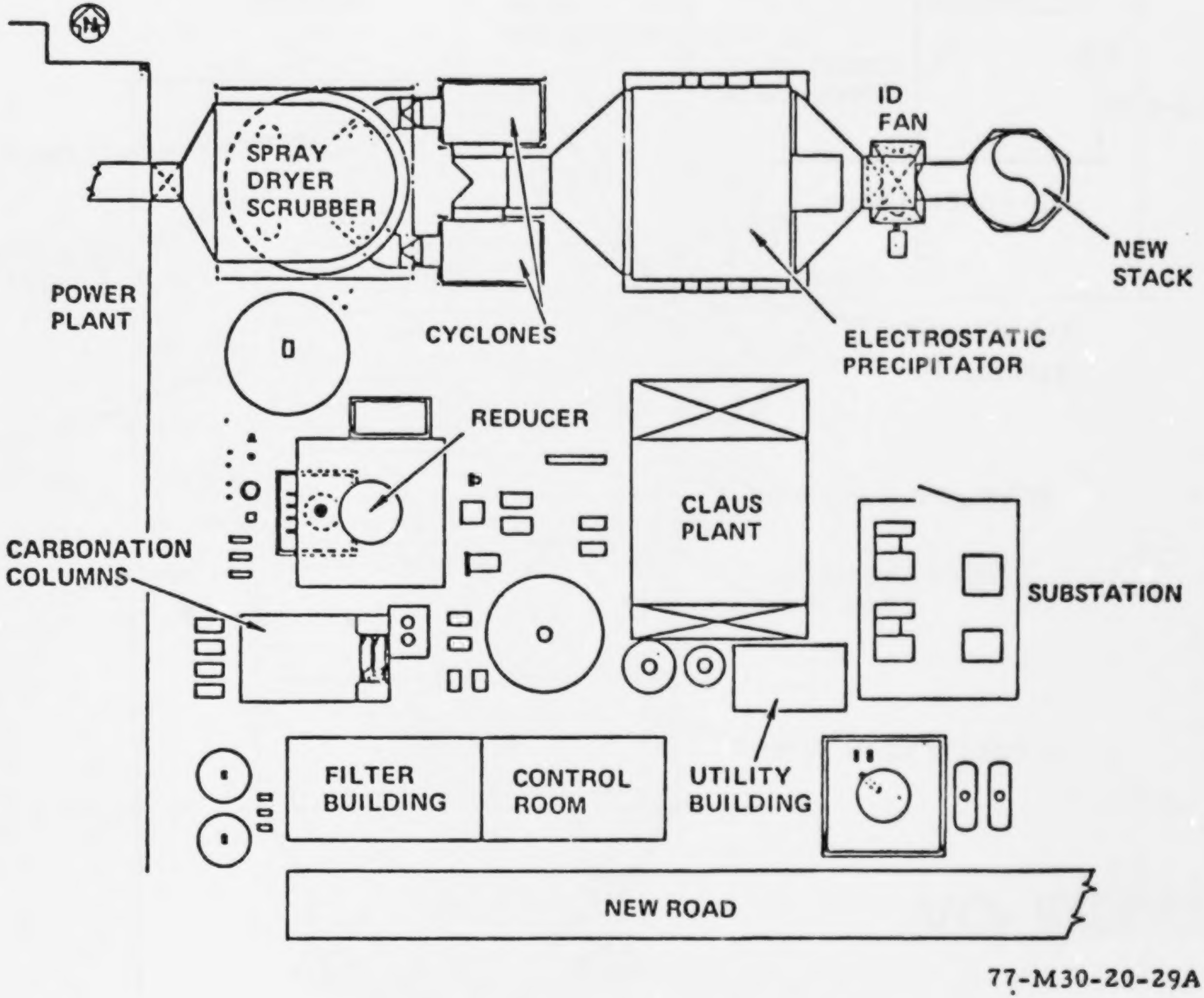


Figure 4. ACP Demonstration Plant Equipment Arrangement

# ACP REDUCER

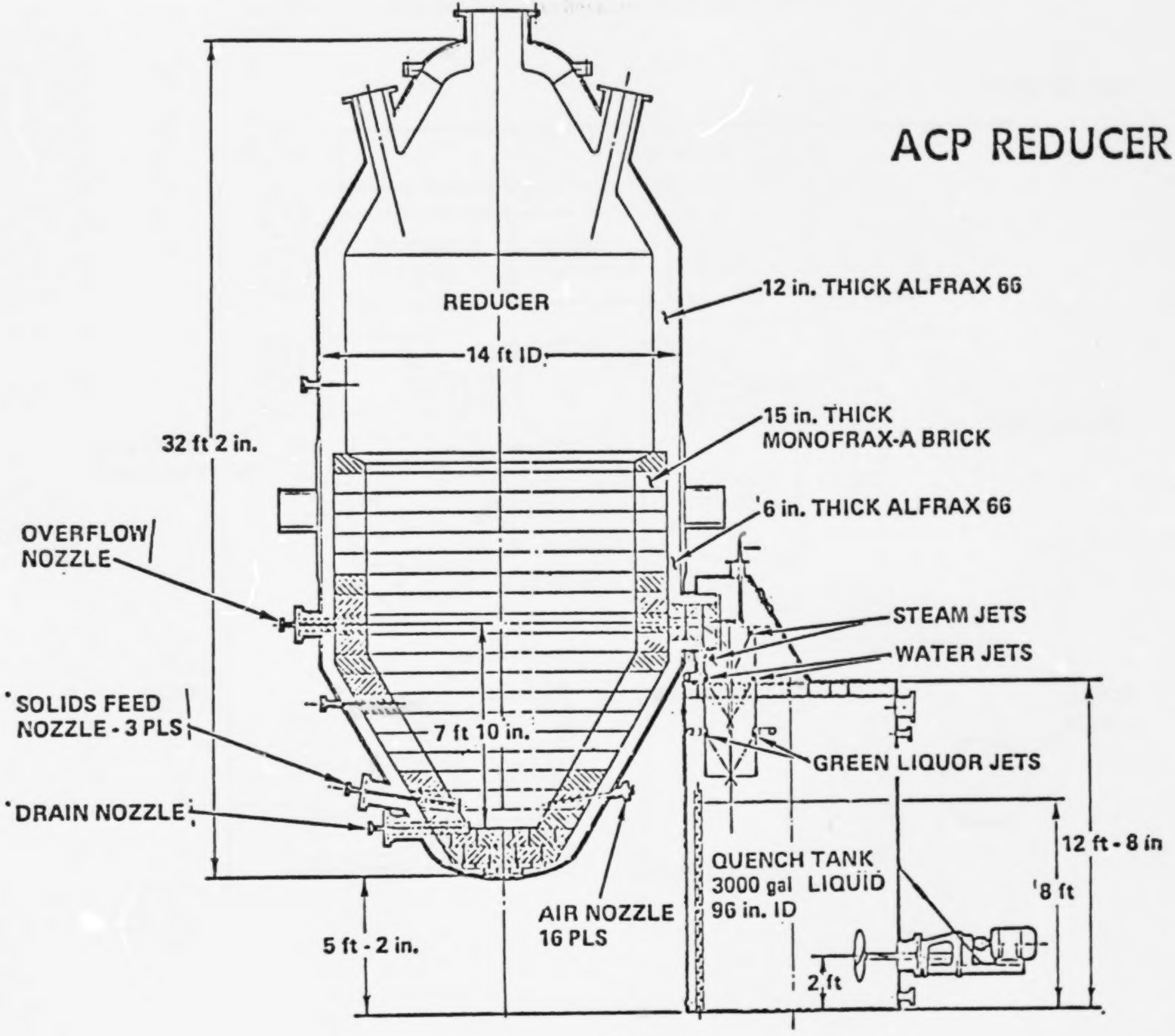


Figure 5

## ACP DEMONSTRATION PLANT
## FLUE GAS TRAIN ELEVATION

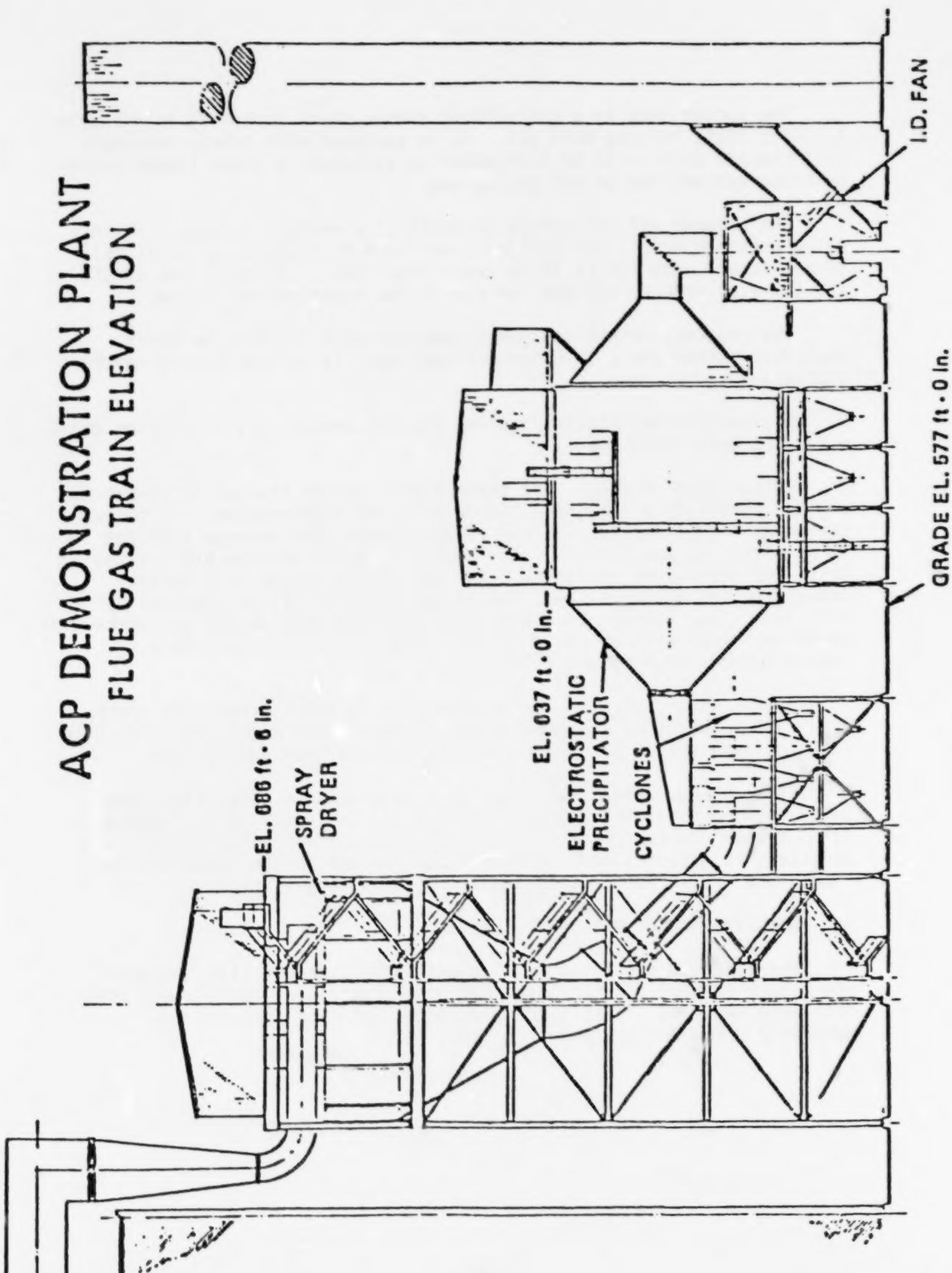


Figure 6

The quench tank is a cylindrical carbon steel tank 8-ft in diameter by 12-ft high, holding 4500 gal. It is equipped with triply redundant melt shatter jets, a 10 hp side-entering agitator, a green liquor recirculation system, and an off-gas system.

The reducer off-gas system consists of a venturi scrubber (40-in. water pressure drop), gas cooling tower (a 4-ft diameter by 12-ft tall packed tower), and fan (a 40 hp centrifugal fan). It cools and scrubs the $CO_2$-rich reducer off-gas for use in the regeneration system.

The reducer preheat equipment consists of a 7.5 million Btu/h dual-fuel burner and a 15 hp centrifugal fan; it is used during reducer startups.

The reducer auxiliaries include the air heater, a 1.75 million Btu/h oil-fired heat exchanger.

Green Liquor System: The green liquor system is used to remove the ash and carbon from the green liquor prior to regeneration. It contains the green liquor cooler, the ash filter system, the storage tank and surge tank, and auxiliaries. The cooler is a 2.2 million Btu/h titanium plate-and-frame heat exchanger. The ash filter system is a rotary vacuum precoat filter system; the filter drum is 3-ft in diameter by 2-ft long. The storage tank and surge tank are both 22,000 gal tanks made of carbon steel with an epoxy lining. The auxiliaries include a liquid cyclone, pumps, and agitators.

Regeneration System: The regeneration system contains the sieve-tray towers and other equipment used to convert the green liquor sulfide solution into sodium carbonate solution and hydrogen sulfide gas.

Claus Plant: The Claus plant is a skid-mounted, shop-fabricated unit. It processes the hydrogen sulfide gas generated in the regeneration system and converts it into 14 tons/day of elemental sulfur. In addition, it produces 6200 lb/h of steam for use in the Demonstration Plant, and its incinerator treats the plant vent gas streams.

## F. UTILITY AND OFF-SITE REQUIREMENTS

There are 12 plant inputs, 7 plant outputs, and 4 site features which must be provided for under the general topic of Utility and Off-Site Requirements. These inputs, outputs, and site features are described below and are shown on Table III.

## TABLE III

### DEMONSTRATION PLANT
### UTILITY AND MATERIAL REQUIREMENTS

| | | | | | |
|---|---|---|---|---|---|
| ELECTRICAL POWER | 2,788 kWh/h | ⇨ | FUEL GAS SYSTEM 100 100 MWe | | |
| PROCESS WATER | 2,565 gal/h | ⇨ | | | |
| ELECTRICAL POWER | 716 kWh/h | ⇨ | REDUCTION SYSTEM 200 + GREEN LIQUOR SYSTEM 300 + CARBONATION SYSTEM 400 | | |
| COOLING WATER (70 - 88°F) | 93,060 gal/h | ⇨ | | ⇨ COOLING WATER RETURN | 93,900 gal/h |
| COKE | 1,760 lb/h | ⇨ | | | |
| MAKE-UP SODIUM CARBONATE | 201 lb/h | ⇨ | | ⇨ ASH TO DISPOSAL | 560 lb/h |
| PROCESS WATER | 2,935 gal/h | ⇨ | | | |
| DIATOMACEOUS EARTH FILTER PRECOAT | 20 lb/h | ⇨ | | | |
| NO. 2 FUEL OIL | 27 gal/h | ⇨ | | | |
| ELECTRICAL POWER | 99 kWh/h | ⇨ | CLAUS PLANT SYSTEM 500 | ⇨ SULFUR | 1,128 lb/h |
| NO. 2 FUEL OIL | 44 gal/h | ⇨ | | | |
| ELECTRICAL POWER | 168 kWh/h | ⇨ | GEN. PLANT SYSTEM 1-99 | | |
| PROCESS WATER | 168 gal/h | ⇨ | | | |
| SULFURIC ACID | 4 gal/h | ⇨ | | | |

## 1. Plant Inputs

### a. Main Water Supply

The main Demonstration Plant water supply provides the process water and cooling water. All of this water will be obtained from the Huntley cooling water inlet canal (tunnel). The pumps, screens, filters, transfer lines, and valves required to obtain this water and bring it to the use points will be installed. The nominal flow rate of the main water supply will be 1650 gal/min, with the cooling water temperature rise limited to 18°F. The water supply will be provided by two 2,000-gpm pumps, one a spare.

Process Water: The Demonstration Plant will have a maximum usage rate of 95 gal/min of process water, which will be used primarily to make up the scrubbing solution and to wash filter cakes. Almost all of this water will be used up, mostly by evaporation.

Cooling Water: The Demonstration Plant will have a maximum cooling water usage rate of 1550 gal/min. All of this water will be returned to the river, along with about 15 gpm of process water.

### b. Fire Protection Water Supply

The Fire Protection Water Supply will be tied into the Huntley Plant Fire Protection System. Sprinkler protection will be provided for the control room and other buildings, and four 500-gpm (nominal) hydrants-hose reels will be installed, one at each corner of the Demonstration Plant site.

### c. Potable Water Supply

Potable water will be taken from within the Huntley Plant and will be used to make up the steam generator feed water and to service the change rooms and lavatories. The maximum steady usage rate (for the steam generator) is 2.8 gal/min.

### d. No. 2 Fuel Oil

A 20,000-gal oil storage tank will be installed. Usage rates will be 1.2 gpm during steady-state. A cold startup will require about 2,500 gal over a period of about 44 hours.

### e. Propane

Propane will be used to cure the reducer refractory and to start up the Claus plant. Two 1000-gal propane tanks and a propane vaporizor will be provided.

f. Petroleum Coke

The Demonstration Plant will be designed to use petroleum coke as the reducing agent, although tests with coal will also be performed. The coke supply will be received in covered hopper trucks and stored in the 100-ton coke hopper. The maximum usage rate will be 1760 lb/h.

g. Coal

The power plant coal will be used as the reducing agent in some tests. This coal will be provided from Niagara Mohawk coal pile. Crushing and grinding will be accomplished prior to loading in the 75-ton coal surge hopper. The maximum usage rate will be about 2000 lb/h.

h. Electrical Power

Electrical power at 23 kV will be supplied from the Niagara Mohawk underground electrical distribution system to the Demonstration Plant substation. The total connected load is 4,650 kW, and the maximum process usage rate will be 3,771 kW.

An emergency electrical supply at 4160 V will be supplied from the Huntley reserve service. Capacity will be limited to 500 kVA, but is sufficient to safely maintain the Demonstration Plant in a standby or safe shutdown mode.

i. Carbonate Make-up

The carbonate make-up rate will be 201 lb/h. Sodium carbonate will be trucked onsite in covered hopper trucks and loaded into the Demonstration Plant make-up system. At start up, 400,000 lbs will be required.

j. Sulfuric Acid

Sulfuric acid will be used to neutralize the chloride purge stream; about 4 gal/h will be needed.

k. Diatomaceous Earth

Diatomaceous earth will be used as a precoat material for the ash filter; 20 lb/h will be used.

l. Flue Gas

The flue gas will be taken out of the Unit 66 duct above the power plant roof and ducted east over the roof of Unit 66 and then down and into the spray dryer scrubber. A shutoff damper will be installed in the Demonstration Plant duct.

## 2. Plant Outputs

### a. Water

The plant discharge water will be made up of the cooling water return, the neutralized chloride purge stream, steam generator effluents, and surface drain streams. The total steady flow rate will be 1565 gpm, most of which will be cooling water. All of this water will be discharged into the 42-in. water drain line which runs underground north of the Demonstration Plant site.

Steam Generator Effluents: The Claus plant steam generator will require a feedwater conditioning system which will use a demineralizer. The demineralizer regeneration system liquid effluents will be disposed of by neutralizing them in the chloride purge stream system and disposing of them along with the neutralized chloride purge stream.

The steam generator blowdown of 30 gal/h will also be disposed of in the 42-in. drain line.

Drains and Storm Sewer: The storm sewer, snow-removal sewer, and other surface plant drains will all be discharged into the underground 42-in. line. No process drains, wash streams, etc., will be discharged into surface drains; they will all be accommodated within the process itself.

### b. Sanitary Sewer

The lavatories, change room, and drinking fountain drains will be discharged into the 6-in. pressurized sewer line running underground near the Demonstration Plant site.

### c. Filter Cake

There are two filter cakes discharged from the Demonstration Plant: the ash filter cake and the leaf filter cake. It is planned to discharge both cakes into a common hopper and dump them on the plant coal pile. (Tests have shown that the mixture of fly ash and filter cake has no sulfide odor.)

There will be a maximum of 455 lb/h of ash filter cake and 105 lb/h of leaf filter cake.

### d. Stack Gas

The stack gas will be discharged through the 200-ft high, 14-ft ID, self-supporting steel Demonstration Plant stack at a maximum rate of 410,000 scfm at a minimum temperature of 170°F.

### e. Claus Plant Tail Gas

When the Demonstration Plant scrubber is in operation, the Claus Plant tail gas will be discharged into the scrubber inlet. When the scrubber is not in operation, the tail gas will be ducted into the main Unit 66 outlet duct for disposal to the main Huntley stack. The tail gas will have a maximum flow rate of 5150 scfm (70°F), will contain up to 0.18% $SO_2$, and will have a maximum temperature at the Unit 66 duct of 600°F.

### f. Air Heater Exhaust Gas

The reducer air heater will burn No. 2 fuel oil. The exhaust gases from this heater burner will be vented to the atmosphere through its own stack. The gases will be typical combustion gases, at a maximum flow rate of 980 scfm (70°F) and a temperature of 800°F.

### g. Sulfur

The sulfur produced in the Demonstration Plant Claus will be stored in molten form in a sulfur pit and will be shipped out periodically in tank trucks. The maximum rate of production will be 13.5 short tons/day.

## G. SPECIAL PLANT FEATURES

The Demonstration Plant is designed as a test facility with more test instrumentation and fewer automatic control systems than would be planned for a normal "$n^{th}$" plant.

The Demonstration Plant design includes a large number of redundant equipment items, including all key pumps, heat exchangers, and blowers, and completely redundant carbonator and crystallizer columns. Also, titanium has been specified for the thin sections of the plate and frame heat exchangers and Incoloy 800 for the decomposer shell. In addition, the use of the plate and frame heat exchanger design will make cleaning of these components less labor intensive.

The Demonstration Plant is designed to use petroleum coke as the reducing agent, but the process features and components needed for tests using coal as the reducing agent have been included.

The present design uses cyclones and an electrostatic precipitator to collect the spent absorbent generated in the spray dryer scrubber. These two collectors could both be replaced with a baghouse dust collector with no significant change in performance or cost.

# IV. LARGE PLANT COST PROJECTIONS

## A. PROCESS DESCRIPTION FOR 500-MW AND 1000-MW PLANTS

A typical 3.5% sulfur Kentucky coal was selected as a reference coal for use in the power plant and also as the reductant for sodium sulfite and sulfate in the spent absorbent. A typical flue gas composition was also selected. The process is essentially the same as in the Demonstration Plant.

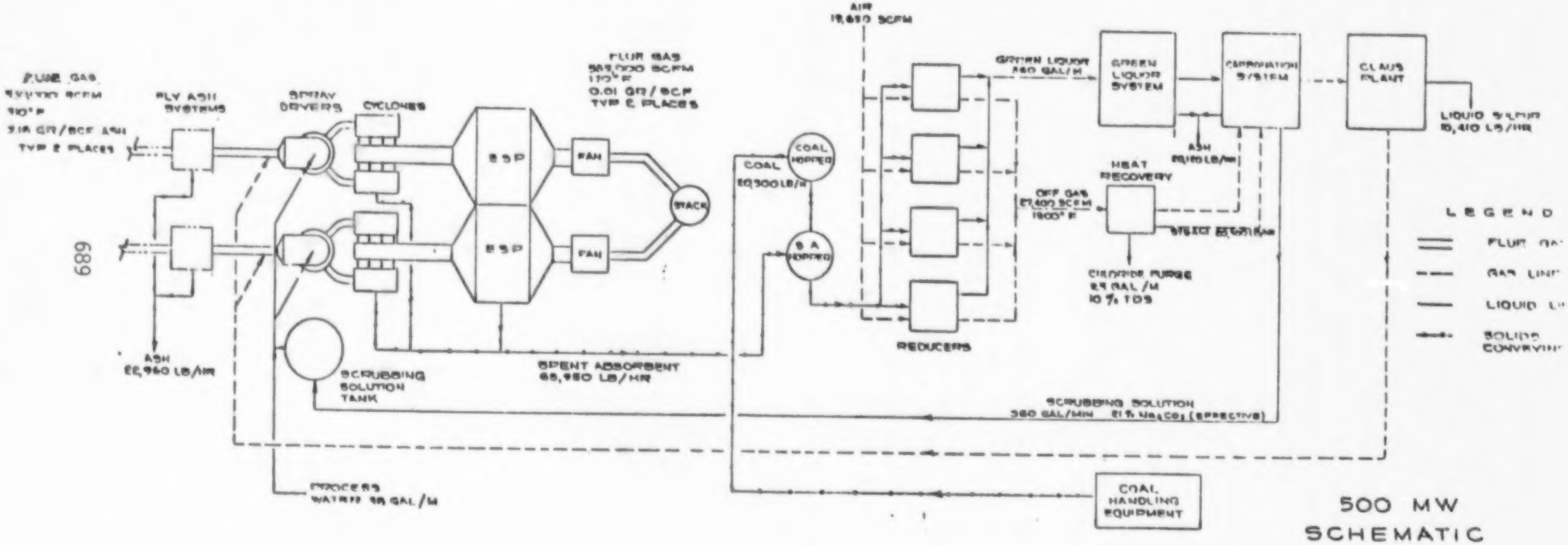
## B. LARGE PLANT DESCRIPTIONS

### 1. 500-MWe Plant

The 500-MWe plant contains two parallel gas scrubbing trains, four parallel spent absorbent molten salt reducers, and single green liquor, carbonation, and Claus plant systems and is shown on Figure 7. The plant design basis is 1,060,000 scfm of flue gas, 3.16 grain/scf of entering fly ash and 22,760 lb/h of entering $SO_2$, with 90% of the $SO_2$ to be removed.

Each of the gas scrubbing trains consists of fly ash collection cyclones, a 52-foot diameter spray dryer scrubber with 5 spray machines, an electrostatic precipitator, and an air foil type induced draft fan with inlet vane control. The gas scrubbing trains share a common stack. In each train, flue gas flows at a rate of 530,000 scfm with a fly ash loading of 3.16 grain/scf, $SO_2$ concentration of 2200 ppm, and a temperature of 310°F through the fly ash collection cyclones, where 80% of the ash is removed, reducing the particle loading to 0.63 grain/scf before the gas enters the spray dryer. The flue gas stream and 20,000 scfm of Claus plant tail gas (the tail gas flow is equally divided between the two spray dryers) are contacted with 198 gal/m of scrubbing solution. The sodium carbonate reacts with and neutralizes 90% of the incoming $SO_2$, and the heat from the flue gas evaporates the water from the droplets, forming dry particles (spent absorbent) made up of a mixture of sodium sulfite, sodium sulfate, sodium carbonate, and agglomerated ash. The scrubbed flue gas leaves the dryer at a flow rate of 585,000 scfm, $SO_2$ concentration of 220 ppm, a temperature of 170°F, and 6.88 grain/scf of spent absorbent, and enters a two-stage particle collection system consisting of cyclones and an electrostatic precipitator. Approximately 34,475 lb/h of spent absorbent are removed by the cyclones and precipitator, reducing the outlet loading to 0.01 grain/scf in each gas train. The spent absorbent is conveyed by a negative pressure pneumatic system into a storage hopper. The flue gas flows from the precipitator through an ID fan operating at 30 in. of water pressure drop, and into the common stack.

The sodium sulfite and sulfate contained in the spent absorbent are reduced to sodium sulfide with coal in a molten pool of sodium sulfide, sulfate, and carbonate at 1800°F. Four parallel reducers, each with a



500 MW SCHEMATIC

Figure 7

16-ft internal diameter, reduce the 68,950 lb/h of spent absorbent with 20,500 lb/h of coal. The off-gas from each reducer is combined and flows at a rate of 27,400 scfm through a heat recovery and particle scrubbing system where 20,000 lb/h of 150 psig steam are generated. Approximately 25 gal/m of a stream containing 10 wt % sodium carbonate, sulfate, and chloride is purged from the regeneration loop. Approximately 4,910 scfm of air is compressed, heated to 1000°F by interchange with the reducer off-gas, and fed to each of the reducers. The molten mixture (melt) of sodium sulfide, sulfate, and carbonate, along with ash and unreacted carbon, flows from the reducer and falls by gravity into a quench tank filled with an aqueous slurry of dissolved salt and suspended ash and carbon. The melt is shattered by steam and liquid jets before contacting the quench liquid. The liquid in the quench tank (green liquor) is pumped from each tank (at a rate of 90 gal/m) into the green liquor and carbonation systems.

The sulfur contained in the green liquor reacts under countercurrent contact conditions with the $CO_2$-rich reducer off-gas to produce an $H_2S$ feed gas stream suitable for the Claus plant, and a scrubbing solution having an effective sodium carbonate concentration of 21.7 wt %. The Claus plant recovers 10,410 lb/h of commercial grade liquid sulfur. The total amount of ash removed from the aqueous stream is 20,120 lb/h of ash; the cake contains 50 wt % water.

The raw material and utility usage rates for the 500 MW plant are listed in Table IV.

### 2. 1000 MWe Plant

The 1000 MWe plant contains four parallel gas scrubbing trains, eight parallel spent absorbent molten salt reducers, and single green liquor, carbonation, and Claus plant systems. The plant design basis is 2,120,000 scfm of flue gas, 3.16 grain/scf of entering fly ash and 45,520 lb/h of entering $SO_2$, with 90% of the $SO_2$ to be removed.

## C. COST PROJECTIONS

### 1. Plant Costs

Summaries of the capital investment requirements for the 500 MWe and 1000 MWe ACP plants are presented in Table V. The plant costs are based on a fourth quarter 1979 plant startup with the midpoint of construction occurring in January 1978. The direct investment costs for the 500 MWe and 1000 MWe plants are $41,466,000 and $69,336,000, respectively. These are equivalent to $82.90/kW for the 500 MWe plant and $69.3/kW for the 1000 MWe plant. The indirect costs are an additional $15,343,000 and $24,934,000, respectively, for the two FGD installations. The indirect capital costs include (1) charges for engineering design and supervision, and for construction field expense, (2) a charge of 5% of

## TABLE IV.

## ANNUAL RAW MATERIAL AND UTILITY REQUIREMENTS
## FOR NEW 500 MWE AND 1000 MWE ACP FLUE GAS DESULFURIZATION PLANTS

|  | Annual Requirement for 7000 hours/year Operation |  |
|---|---|---|
| Raw Materials | 500 MWe | 1000 MWe |
| Coal, tons | 71,750 | 143,500 |
| Sodium carbonate, tons | 10,500 | 21,000 |
| No. 2 fuel oil (Claus plant use), $10^3$ gal | 2,100 | 4,200 |
| Diatomaceous earth filter precoat, tons | 1,050 | 2,100 |
| Utilities |  |  |
| Electrical power, $10^3$ kWh | 103,250 | 206,500 |
| Cooling water, $10^6$ gal | 4,305 | 8,610 |
| Process water, $10^6$ gal | 155.4 | 310.8 |
| Fly ash disposal, tons | 80,500 | 161,000 |
| Wet ash disposal, tons | 70,700 | 141,400 |
| Sulfur Credit |  |  |
| Sulfur, tons | 36,435 | 72,870 |

## TABLE V

## TOTAL CAPITAL INVESTMENT REQUIREMENTS FOR A NEW 500 MWe & 1000 MWe ACP FLUE GAS DESULFURIZATION PLANT

| | 500 MWe | | 1000 MWe | |
|---|---|---|---|---|
| | $000'S | PERCENT DIRECT INVESTMENT | $000'S | PERCENT DIRECT INVESTMENT |
| Direct Costs | | | | |
| Equipment and Erection | 14,468 | 34.9 | 26,914 | 38.8 |
| Subcontract Equipment | 10,442 | 25.2 | 17,325 | 25.0 |
| General Subcontracts, Buildings, Foundations and Structures | 15,781 | 38.0 | 23,797 | 34.3 |
| Maintenance Materials and Initial Fill | 775 | 1.9 | 1,300 | 1.9 |
| Subtotal Direct Investment | 41,466 | 100.0 | 69,336 | 100.0 |
| Indirect Costs | | | | |
| Engineering Design and Supervision | 1,659 | 4.0 | 2,080 | 3.0 |
| Construction Field Expense | 1,244 | 4.0 | 2,080 | 3.0 |
| Contractor Fees | 2,073 | 5.0 | 3,467 | 5.0 |
| Contingency | 4,147 | 10.0 | 6,934 | 10.0 |
| Subtotal Fixed Investment | 50,589 | 123.0 | 83,897 | 121.0 |
| Allowance for Startup and Modifications | 1,659 | 4.0 | 2,773 | 4.0 |
| Interest During Construction | 4,561 | 11.0 | 7,600 | 11.0 |
| Total Capital Investment | 56,809 | 138.0 | 94,270 | 136.0 |

Basis: Costs are based on plant startup in the fourth quarter of 1979.

the direct investment for contractor fees, (3) a 10% contingency, (4) an allowance for startup and modifications, and (5) a charge of 11% for interest during construction. The total cost for the 500 MWe FGD plant is thus $56,809,000 ($113.5/kW), and the total cost of the 1000 MWe plant is $94,270,000 ($94.3/kW.)

### 2. Operating Costs

The operating costs for the 500 MWe and 1000 MWe FGD plants are presented in Table VI. The annual operating costs are based on 7000 hours/year of operation and projected estimates of the costs of raw materials and utilities for a fourth quarter 1979 plant startup. The number of men per shift required to operate the two plants is 10 for the 500 MWe plant and 16 for the 1000 MWe plant. The operating labor cost is based on 4.5 men/shift position for full coverage.

## TABLE VI

## OPERATING COST ESTIMATES

| | 500 MW ($000) | 1000 MW ($000) |
|---|---|---|
| o RAW MATERIALS | | |
| . SODA ASH AT $90/TON | 461 | 900 |
| . COKE AT $32/TON | 2,020 | 4,000 |
| . CLAUS CATALYST | 32 | 70 |
| . FILTER PRECOAT AT $115/TON | 121 | 230 |
| o UTILITIES | | |
| . FUEL OIL AT $0.40/gal | 840 | 1,600 |
| . RAW WATER AT $0.02/1000 GAL | 86 | 170 |
| . TREATED WATER AT $0.50/1000 GAL | 78 | 150 |
| . ELECTRICITY AT $0.025/kWh | 2,582 | 5,000 |
| o MAINTENANCE MATERIALS AND LABOR | 1,628 | 2,700 |
| o OPERATING LABOR AND SUPERVISION AT $12.50/h | 792 | 1,200 |
| o PLANT OVERHEAD | 1,210 | 1,950 |
| o ADMINISTRATIVE OVERHEAD | 240 | 450 |
| o CAPITAL CHARGE | 8,460 | 14,050 |
| GROSS ANNUAL COSTS | 18,550 | 32,470 |
| o SULFUR CREDIT AT $45/TON | 1,640 | 3,280 |
| NET ANNUAL COSTS | 16,910 | 29,190 |
| ANNUALIZED COST (MILLS/kWh) | 4.8 | 4.2 |

# STATUS OF THE CATALYTIC OXIDATION (CAT-OX) FLUE GAS DESULFURIZATION SYSTEM

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## ABSTRACT

This paper is a summary of the experience gained and problems encountered during the Cat-Ox demonstration program. The paper briefly defines the process design and outlines the construction history of Cat-Ox. However, the focus of the paper is on operating experience and problems encountered which led to the decision to discontinue the demonstration program. Brief summaries of test results and conclusions derived from the demonstration program are provided. Detailed test results from the baseline test program, acceptance testing, ESP testing, transient testing, and other special tests and studies associated with the Cat-Ox system are reported elsewhere in documentation cited by the paper.

# STATUS OF THE CATALYTIC OXIDATION
# (CAT-OX) FLUE GAS DESULFURIZATION SYSTEM

## GENERAL

The Cat-Ox$^{T.M.*}$ flue gas desulfurization system controls $SO_2$ emission by catalytic oxidation of the $SO_2$ to $SO_3$. The $SO_3$ is then collected from the flue gas as sulfuric acid in an absorption tower.

The addition of the Cat-Ox system to The Illinois Power Company (IPC) Unit No. 4 boiler (100 Mw) at the Wood River Station required the interruption of the exhaust flue gas flow at the entrance to the stack, diversion through the process, and return of the cleaned gas to the stack. Boiler operations and particle removal are independent of the rest of the Cat-Ox system, and can operate during Cat-Ox maintenance outages by virtue of a gas by-pass around the Cat-Ox system.

Key objectives of the Cat-Ox system are: (1) to remove 85 percent of the $SO_2$ from the flue gas, and (2) to remove essentially 100 percent of the particulate matter from the flue gas. The system is designed to achieve these objectives over the normal boiler load range.

The Cat-Ox system and boiler are schematically shown in Figure 1. The process consists of six basic steps which are described as follows:

1. Flue Gas Cleaning - by means of an electrostatic precipitator
2. Flue Gas Reheating - with a Ljungstrom regenerative gas heat exchanger and an external oil-fired burner
3. Conversion of $SO_2$ to $SO_3$ - in a catalyst bed
4. Heating Recovery - through the Ljungstrom regenerative gas heat exchanger
5. Sulfuric Acid Collection - by condensation in a packed bed absorbing tower with external shell and tube heat exchangers
6. Product Storage and Loading - where cooled product acid at 60° Baume´ is collected in two 442,000 gallon steel storage tanks. Acid loading pumps and tank car loading facilities are provided adjacent to the storage tanks.

Additional more detailed descriptions of the process can be found in the documentation cited at the end of this paper.

The normal operating ranges of important process variables are indicated in Table 1.

## Background

In early 1970, Illinois Power Company began negotiations with the Office of Air Programs of the U.S. Environmental Protection Agency to jointly fund a demonstration unit on the 100 Mw Unit #4 at the Wood River Power Station of IP. This

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[*] Cat-Ox$^{T.M.}$ is a proprietary designation of Monsanto Company.

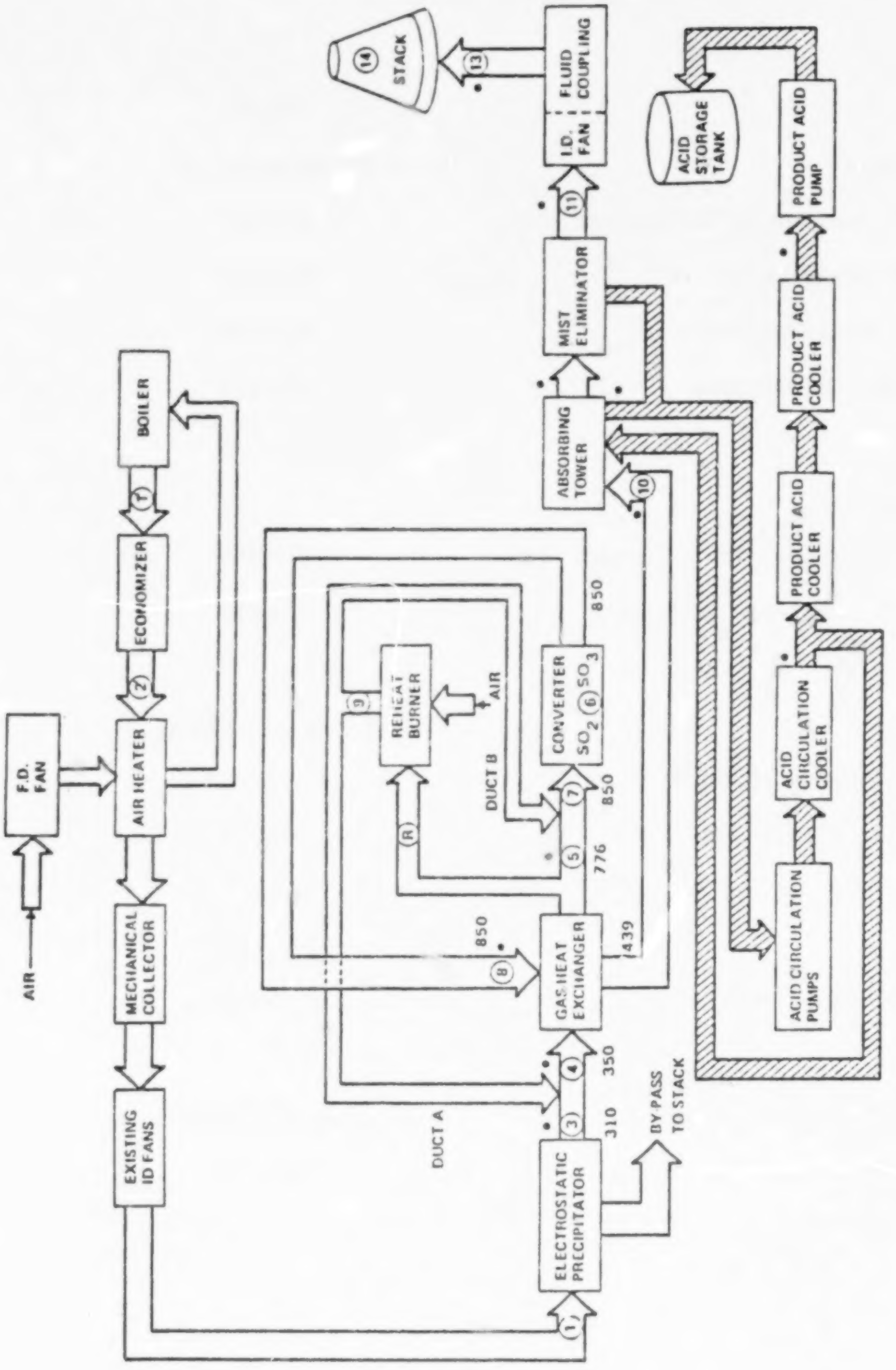

FIGURE 1. STEAM GENERATOR AND CAT-OX PROCESS

## TABLE 1. NORMAL OPERATING RANGE OF IMPORTANT VARIABLES IN THE CAT-OX SYSTEM

| VARIABLE | VALUE |
|---|---|
| Flue Gas Temperature | Temperature, F |
| Flue Gas to Gas Heater Exchanger | 340-360 |
| Flue Gas to Converter | 825-875 |
| $SO_3$ Gas to Absorbing Tower | 420-440 |
| Gas from Mist Eliminators | 235-255 |
| Acid Temperature | |
| Acid to Acid Circulation Coolers | 275-290 |
| Acid from Product Acid Coolers | 70-110 |
| Flue Gas Pressure | Pressure, Inches w.c. |
| $SO_3$ Gas from Converter* | -11 to -19 |
| Gas from Mist Eliminator* | -41 to -53 |
| Acid Flow | Flow, GPM |
| Acid to Absorbing Tower | 1700-2100 |
| Flue Gas Composition | $SO_2$, PPM Volume |
| Gas to Stack | 300-400 |

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*Full Load

project was jointly funded by the U.S. EPA and by Illinois Power Company in an effort to advance the technology of sulfur dioxide removal by developing a system that would produce a usable by-product in the form of sulfuric acid.

Unit #4 at Wood River normally burned approximately 275,000 tons of coal per year with an average sulfur content of 3.1 percent. Based on these figures, the Cat-Ox system should produce about 25,000 tons per year of 78 percent concentration sulfuric acid. Formal negotiations for installation of the Cat-Ox demonstration system were started with the preparation of a preliminary study by Monsanto Enviro-Chem in February 1970. The U.S. Environmental Protection Agency contracted with Illinois Power Company on 26 June 1970 to engage Monsanto Enviro-Chem to design and construct the Cat-Ox demonstration unit. Capital funding was shared approximately equally between the Environmental Protection Agency and Illinois Power Company. In addition, Illinois Power Company assumed the financial obligations of providing the necessary utilities and of maintaining and operating the Cat-Ox system for a period identified in the contract.

## Initial Operating Experience

Construction of the Cat-Ox system started in January 1971 and the associated Research-Cottrell precipitator designed for Cat-Ox was completed and placed in service in January 1972. Initial start-up of the sulfur removal equipment occurred on 4 September 1972 using natural gas for the in-line reheat burners. The system was operated for approximately 444 hours during the entire testing period. Because of the unavailability of natural gas, it was necessary to try to operate the in-line reheat burners on #2 fuel oil. In October 1972, testing with fuel oil was started. The testing period and modifications continued during the period of November 1972 to June 1973. During this test period, it became apparent that an external combustion chamber for reheating would be required to maintain satisfactory and continuous operation when using oil as the reheat fuel. This was necessary because the difficulty in achieving proper ignition of the in-line burners on #2 oil would cause excessive contamination of the catalyst. Also, these burners could not be maintained properly. Since this would not be acceptable, it was agreed to construct the external reheat burner using #2 fuel oil with the required heat being ducted into the system at the present location of the in-line burners.

Before installation of the external heater, a performance guarantee test was run and satisfactorily completed using #2 oil as fuel in the in-line heaters in July 1973. The Cat-Ox operation that took place during this testing period increased the total operating time on the Cat-Ox system to approximately 602 hours. During the month of August 1973, the Cat-Ox system was de-activated and laid up in such a manner as to allow for a long outage so the external burner could be installed. The installation of the external burner was completed in April of 1974 and attempts were made to place the unit back in operation.

Operation after Combustion Chamber Installation. On 8 April 1974, the pilot gas burner was lit off in the external combustion chamber, and a drying out process for the refractory in the combustion chamber was started shortly afterwards. On 15 April, testing of the external combustion chamber using fuel oil was started. On 18 April, an attempt was made to transfer acid to the absorbing tower but it was found that the acid line was plugged and acid could not be transferred. This product acid line from the storage tanks to the absorbing tower was found to be plugged with solidified corrosion products, and necessitated cutting and flushing the line until cleared.

During the period from 2 May through 13 May, a number of repairs to miscellaneous equipment were made including repair of acid line leaks, and leaks in the absorbing tower lead lining as well as repairs to the catalyst handling system so that additional catalyst could be added to the beds to top them off.

On 23 May 1974, repairs were started on the leaks in the absorbing tower using a potassium silicate solution.

On 3 June 1974, the blanking plates were removed and the Cat-Ox system prepared for start-up, with acid being added to the absorbing tower. On 4 June, the external combustion system was placed into operation and on 5 June warming up of the Cat-Ox system was started. In the period from 7 June through 27 June 1974, attempts were made to circulate acid through the absorbing tower but acid cooler leaks, bearing failures in acid recirculation pumps, and broken impeller problems in the acid pumps caused shutdowns and resulted in considerable maintenance being done to these items during the entire period.

On 28 June, the blanking plates were installed back in the inlet and outlet ducts. More leaks were found in one of the acid coolers and additional tube plugging in that cooler was required. On 10 July 1974, a piping change in the cooling water piping to and from the induced draft fan lube oil cooler was started. This was necessary to eliminate some of the temperature control problems of the oil from the lube oil cooler.

During the period of 29 July through 13 August 1974, the acid recirculation pumps were rebuilt and a new casing and impeller was installed on the product acid pump. Also additional tubes were plugged in one of the acid coolers.

On 14 August, all three acid pumps were operated for checkout and the blanking plates were pulled and the reheat burner system placed into operation. On 15 August, the reheat burner temperature was at 800° F, but there were problems in the air dampers on the reheat burner system. In the afternoon, it was necessary to shutdown to repair a leak in the acid product line and to work on the dampers. The reheat burner system was placed back into service in the evening of 15 August and the temperature was held at 1050° F to dry out the combustion furnace. The operation of the reheat burner system was continued on 16 August, but a leak in the acid discharge header from the recirculation pump caused a shutdown about 5:50 p.m. and on 17 August, the blanking plates were reinstalled in the inlet and outlet ducts.

During the period of 17 August through 28 August, a number of repairs were made to the acid coolers and the acid recirculation system. On 17 September 1974, a masonry contractor removed damaged refractory brick from the combustion chamber of the reheat burner system. During the period of 17 September through 25 October, substantial repairs were made to two of the acid coolers. On 25 October, a fire was lit in the reheat burner system to dry out the refractory in the combustion chamber. This drying out continued through 31 October and on into the first part of November. On 2 November 1974, the drying out of the reheat burner combustion chamber was completed and work was done on a new design connection at the transition point where the duct from the reheat burner system went into the reheat B area.

On 3 December 1974, a steam coil hot air heater was placed in service to keep moisture out of the catalyst beds. On 10 December 1974, a hydrostatic test was conducted on the product acid line to the storage tanks; and during the period of 11, 12 and 13 December, flushing and drying of the product acid line was done. During the rest of December and January, 1975, only minor operations were conducted to test the ID fan. Meanwhile, work continued on the new design connection at the "B" transition.

On 28 January 1975, a small gas fire was placed in the reheat burner combustion chamber to dry out and cure the refractory. This continued through 30 January at which time the temperature was raised to 1800° F to check out the combustion chamber. At this time, testing the burner on the fuel oil was started. The testing of the combustion chamber on fuel oil continued through 3 February but difficulty was experienced with the gas pilot torch. Also on 3 February, acid was transferred from the storage tanks to the absorbing tower to fill the coolers, pumps, and acid lines for tests. On 4 February, all three acid recirculation pumps were run with no leaks observed. Reheat burner chamber checkout continued. On 6 February, a tube leak occurred in one of the acid coolers, and it had to be isolated. On 7 February, the reheat burner checkout continued with more reliability of the pilot being experienced. On 10 February, the reheat burner was fired successfully several times but then difficulty occurred on the air/oil differential control. On 25 February, acid was transferred back from storage in order to test the acid coolers and pumps. On 26 February, the fuel oil fire was established in the reheat burner and the acid pumps were started up but leaks appeared in the acid cooler differential control. On 25 February, acid was transferred back from storage in order to test the acid coolers and pumps. On 26 February, the fuel oil fire was established in the reheat burner and the acid pumps were started up but leaks appeared in the acid coolers so the reheat burner was shutdown and the acid coolers drained.

During the period of 27 February through the end of March, acid cooler work was continued and on several occasions the acid coolers were tested and additional leaks were found resulting in more repair work. On 8 April 1975, all acid from the north storage tank was pumped to the south acid storage tank. Also an attempt was made to pump acid from the absorbing tower back to the storage tank but difficulty was experienced in the product acid line.

At this point in time, Illinois Power requested that the costly attempts to repair Cat-Ox be stopped pending further agreement on how to proceed with the demonstration program. Toward this end, EPA contracted Dow Chemical Company and Radian Corporation with support from MITRE/METREK to investigate the required means and costs to refurbish Cat-Ox as well as the costs and benefits of continuing the demonstration program.

On 12 May, the product acid line was flushed with water and blown dry with air. On 14 August 1975, the catalyst from the #1 bed of the converter was conveyed to the storage tank in preparation for screening.

During the period of 7 August through 22 August all of the catalyst was transferred through the sifter for cleaning purposes and replaced back in the beds. When it was completed, it was found that the #8 bed was down approximately ten feet. After an inspection, it was found that large quantities of the catalyst had fallen down between the beds and into the gas spaces of the ducts. This area was cleaned and approximately 100 to 200 bushels of catalyst was removed from these spaces.

On 22 September 1975, the absorbing tower was opened up and the mist eliminator wash system placed into operation. The upper and lower mist eliminator tube sheets were completely washed down and all of the acid area of the absorbing tower was washed and cleaned.

Through the period of 29 September through 3 October, the Cat-Ox system was opened up for inspection by personnel of the Dow Chemical Company and MITRE Corporation.

On 17 October, the Cat-Ox system was laid up and all cooling water systems drained for freeze protection.

## CURRENT STATUS OF PROCESS

### Equipment Status

In June of 1975, Monsanto Enviro-Chem provided Illinois Power with a procedure for mothballing a Cat-Ox unit. As much as could be done, Illinois Power Company completed the lay up procedure on the Cat-Ox equipment. There was some equipment, because of its condition and its need for extensive maintenance or complete replacement, that kept it from getting the complete mothballing treatment.

During this inactive or mothballing stage, there was some equipment that required periodic operation such as turning over of the induced draft fan and rotating the Ljungstrom air heater. In the process of operating the induced draft fan, a leak occurred in the lubricating oil system and the oil was lost from the system. Because of the extensive repairs that would be required, the fan is being left in the inactive state. The same type of situation occurred in regard to the Ljungstrom air heater. A periodic rotation of the air heater was performed, but a leak developed in the oil line for lubrication so it became necessary to stop the periodic operation of this piece of equipment also. It is felt that the non-operation of the air heater will not be any problem to it since there are periods of time in which the air heater can be left without operation and not cause any problems with the bearings or the air heater unit itself. In the case of the induced draft fan, the condition of the bearings and the shaft on that fan are such that if it ever did become necessary to operate the unit extensive repairs would be required on the fan.

The major sections of the Cat-Ox system such as the two acid storage tanks and the absorbing tower have all been completely cleaned out and dried out so that there should not be any acceleration of corrosion in this equipment. The converter has been left with the catalyst in place, and there is a steam heated system supplying warm air into the converter to keep the catalyst dry. It would be difficult in making an evaluation of the Cat-Ox in its current stage to enumerate the condition of all of the equipment without becoming too detailed for this particular paper. There have been several evaluations made on the Cat-Ox system that do give detailed conditions of the equipment and if such detail is required then those reports should be consulted.

### Tests Accomplished

The Baseline Test Program to characterize the boiler prior to the installation of Cat-Ox was performed on schedule and as planned with no significant difficulties. The results of the test program are described in the documentation cited at the end of this paper.

The Monsanto acceptance tests were also completed. These tests brought out some problems in the system (primarily with the internal burners) which were to be resolved prior to the start-up of the demonstration program. IP and Monsanto agreed that the test series was acceptable proof that the system would operate.

The main test program was not completed since the Cat-Ox one-year demonstration program could not be initiated because of the problems encountered. One portion of the test program was completed; it was the first series of ESP tests which are also described in the cited documentation. These tests comprised a series of subsystem (ESP) tests which did not require the operation of Cat-Ox. A number of transient program tests were also performed. These tests were mainly baseline tests to determine the changes that occurred in emissions under normal start-ups and load changes in the boiler. These tests were also performed when Cat-Ox was not in operation.

A corrosion test program was performed at Cat-Ox. While most of the testing was completed under non-operational conditions, some testing was performed under start-up conditions. A study consisting of observations of equipment was also part of the test program.

Official tests scheduled for the external burner were never run. However, MITRE did assist Monsanto and IP on some of the preliminary tests and obtained some initial data.

During the period between May 1974 and April 1975, there were continued attempts to operate the system using the external reheat burners. A number of malfunctions and process component failures occurred which prevented successful completion efforts. The problems included failures of the acid circulation pumps, persistent leaks in acid coolers and circulation system piping as well as burner and burner control problems. After continued efforts to repair and operate Cat-Ox IP stopped further work on the system, taking the position that some basic system changes (especially in the acid cooler area) were required before Cat-Ox could be successfully operated. This position was stated in a meeting between IP, EPA, and MEC held at Wood River on 17 April 1975. Following the meeting, a lay-up procedure provided by Monsanto was put into effect and Cat-Ox was completely deactivated in a manner that was designed to protect the equipment from freeze or corrosion problems. This was completed in October of 1975.

The Environmental Protection Agency then performed and funded a number of technical and economic studies relating to the costs and benefits of continuing the demonstration program at Wood River. The results of these studies led to a decision to discontinue the project.

## CONCLUSIONS DERIVED FROM OPERATING EXPERIENCE

### Conclusions Relating to Process Design

The Cat-Ox pilot plant and prototype plant, the 24-hour acceptance test of the Wood River system, and various other tests and studies indicated that the Cat-Ox process is a technically viable process. Current technology for particle control is capable of meeting the inlet requirements for the Cat-Ox process in either the integrated or retrofit systems. The catalytic converter is capable of greater than 90 percent $SO_2$ to $SO_3$ conversion efficiency. The 77.7 percent $H_2SO_4$ concentration can be maintained during steady state and transient operation. However, one study* indicated that lengthy start-up conditions could result in the generation of dilute hot $H_2SO_4$ which can cause serious corrosion problems within the system.

An economic comparison of Cat-Ox with Mag-Ox and Wellman-Lord/Allied FGD processes showed that the Cat-Ox process required the highest capital investment but that the integrated Cat-Ox had the lowest annual operating costs. The same study indicated that the Cat-Ox process was less sensitive to coal sulfur content than the other processes; however, the Mag-Ox process produced the least impact on the cost of electricity. Although the selling price of the acid and its "saleability" would have a significant effect on the Cat-Ox annualized costs this factor is site specific and could not be factored into the comparison. The primary market for the dilute, impure acid from the Cat-Ox process is the fertilizer industry. This industry consumes over half the sulfuric acid manufactured in the U.S. While the trace elements in the acid produced by Cat-Ox have not been shown to produce detrimental health and environmental effects when used in the agriculture industry, more research is required before any final judgment can be made.

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*Cat-Ox Product Acid Strength Study, The MITRE Corp. M75-88, December 1975.

### Conclusions Relating to the Specific Demonstration

Though the process design appears technically viable, the Wood River demonstration was plagued with numerous operational problems. The problems were related to two basic areas:

- Design. Certain characteristics or requirements of the system and power plant environment were not accounted for or identified in the initial design of the unit.
    - Internal reheat system would not function properly when the system was committed to use oil instead of gas. This resulted in lengthy start-ups.
    - Vibration in the power plant environment was assumed to cause breakage or wear of the graphite heat exchanger (primarily at a metal-graphite contact point in the tube bundle). Acid or water flow may also have contributed to the vibrations.
    - Dilute acid caused by lengthy start-ups resulted in serious corrosion in portions of the system.
    - Inability to isolate some equipment so it could be maintained with the system in service resulted in added shutdowns.
- Operation. Power plant personnel were unfamiliar with chemical plant operations and requirements, although technical direction was provided.
    - Personnel were unfamiliar with the operating and maintenance requirements of special alloys, material, and equipment such as duriron recirculating pumps.
    - Unfamiliarity with acid handling problems resulted in the corrosion of areas in the product handling system.

These problems combined to result in lengthy delays with further compounded the problems. In addition, long periods of shutdown had an adverse effect on the process and caused serious deterioration of some system components. The only system component that was both operational and functioning without problems since its construction was the electrostatic precipitator.

After continued attempts to operate Cat-Ox, IP halted repair efforts on the system and took the position that some basis modifications to the system design were required for the Cat-Ox demonstration to be successfully completed.

A survey of the plant status funded by EPA indicated that the major problems outlined earlier along with system deterioration problems could be solved but would require a major restoration program.

In the interim, IP has chosen to comply with $SO_2$ standards by burning low sulfur coal in the Unit No. 5 boiler, and physical plant arrangement constraints prevent them from employing a different type of coal for Unit 4. Thus, the demonstration program would, therefore, have to be run on low sulfur coal. Though the results based on low sulfur fuel operation would be useful, they would leave many serious questions unanswered about Cat-Ox operability. Hence, continuation of the demonstration would be of very limited use; and accordingly, the program was discontinued.

Discontinuation of the demonstration program neither proves nor disproves the feasibility of the Cat-Ox system. However, some inferences from the experiences indicate that the Cat-Ox system would probably be more desirable in an integrated system application rather than in a retrofit situation. The benefits associated with the integrated system application are:

- The reheat system would not be required.
- There could be more advantageous placement of system components and elimination of long product lines and poor accessibility of some equipment.
- The annual operating costs would be lower for an integrated Cat-Ox.

Furthermore, other more economical regenerable FGD systems have been demonstrated at a more advanced stage for retrofit situations. Little benefit could, therefore, be realized from the large expenditure to refurbish the retrofit Cat-Ox demonstration system.

# CAT-OX DOCUMENTATION AVAILABLE
# FROM THE MITRE CORPORATION

"Management Plan - Test Support for the Cat-Ox Demonstration Program," MTR-6054, July 1971.

"Baseline Measurement Test Plan for the Cat-Ox Demonstration Program," MTR-6053, October 1971.

"Baseline Measurement Test Results for the Cat-Ox Demonstration Program," MTR-6213, June 1972.

"MITRE Test Support for the Cat-Ox Demonstration Program," M73-50, May 1973.

"Test Evaluation of the Cat-Ox High Efficiency Electrostatic Precipitator," M75-51, July 1975.

"Baseline Measurement Test Resulted for the Cat-Ox Demonstration Program," M73-42, April 1973.

"The Cat-Ox Demonstration Program," (presented to the Flue Gas Desulfurization Symposium), M74-106, November 1974.

"Test Evaluation of Cat-Ox High Efficiency Electrostatic Precipitator," M75-51. (EPA-600/2-75-037), July 1975.

"Test Plan for the Cat-Ox Demonstration," M75-59, March 1974.

"Narrative Description of Slides Presented to EPA as Part of the Cat-Ox Survey Task," WP-11262, September 1975.

"Cat-Ox Product Acid Strength Study," M75-88, December 1975.

"Cat-Ox FGD Demonstration Program Final Report-Draft Form," M77-23, July 1977.

# CITRATE PROCESS DEMONSTRATION PLANT
# – A PROGRESS REPORT –

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## ABSTRACT

The Citrate Process Demonstration Plant represents a joint government/industry project for the commercial application of the Citrate FGD Process to an existing 60 MWe coal-fired power generation station. The Citrate Process was developed by the U.S. Department of Interior, Bureau of Mines and pilot tested over a three year period. Pilot testing confirmed process, operational, and performance parameters and established the design basis and engineering criteria for commercial demonstration of the Citrate Process.

This paper discusses the host site, process description, the physical equipment, the operational objectives, the one year demonstration test program, the process environmental and energy impact, and the process economics.

# CITRATE PROCESS DEMONSTRATION PLANT

## – A PROGRESS REPORT –

## INTRODUCTION

The Citrate Flue Gas Desulfurization (FGD) Process was developed by the U.S. Department of the Interior's Bureau of Mines as a means for abatement of $SO_2$ emission discharges from the nonferrous smelting industry. Extensive laboratory bench and field testing spaning a period of almost ten years was culminated with the successful 1000 SCFM (1500 SCFM, maximum) pilot testing of the Citrate Process at a base metal smelter application located in Kellogg, Idaho.

Pilot operation confirmed previous laboratory research that the Citrate Process is capable of greater than 99 percent removal of sulfur dioxide discharge from industrial waste gases. The sulfur dioxide is converted to elemental sulfur with less than 1.5 percent converted to sulfate, regardless of feedgas $SO_2$ and oxygen content.[1] Other pilot tests sponsored by private industry have treated stack gas discharges from a coal-fired industrial steam boiler simulating a utility application.[2]

The successful pilot operations of the Citrate Process on both the smelter and coal-fired industrial boiler applications confirmed feedstock consumption rates, confirmed a $SO_2$ removal efficiency exceeding 95 percent, and established a good record of mechanical and process equipment performance.[3]

Motivated by the success of the pilot tests, the operational and performance parameters were evaluated, characterized, and optimized sufficiently to develop the necessary design criteria to demonstrate citrate technology on a commercial scale.

Hence, plans were initiated by the Bureau of Mines together with the Environmental Protection Agency (EPA) for the design and construction of a commercial scale plant to demonstrate the Citrate FGD Process at power plants burning high sulfur coal fuels. By mid-1976, the Bureau of Mines had executed a cost-sharing cooperative agreement with the St. Joe Minerals Corporation (St. Joe) to construct the planned demonstration plant at St. Joe's G.F. Weaton electric generating station at Monaca, Pennsylvania.

The purpose of the Citrate Process Demonstration Plant is to demonstrate that the process, as developed to its present status at the Kellogg, Idaho Pilot Plant, can operate reliably and efficiently in removing sulfur oxides from flue gases in a commercial installation. In order to achieve this, the Citrate Process is being retrofitted to treat 156,000 SCFM (234,000 ACFM) of flue gas from the coal-burning G.F. Weaton electric generating station.

N.B. – Metric equivalents (SI Units) for quantitative unit - expressed in this paper are listed as an appendix.

Engineering design and construction services for the demonstration project are being provided to the project sponsors under a "turn-key" design/build/operate contract with the Morrison-Knudsen Company, Inc. (M-K) of Boise, Idaho.

## PROGRESS TO DATE

The Citrate Process Demonstration Plant project is divided into four phases:

Phase I – Preliminary engineering and design development necessary to establish a definite construction cost estimate was completed in November 1976.

Phase II – Final engineering detailed design, and equipment procurement commenced March 1977. Site preparation, foundations, erection of structural steel and mechanical process tie-ins with the existing power station began July 1977. Most major equipment including the absorption column, sulfur precipitation reactors, and process pumps will be received and installed this winter (November 1977 - February 1978). Completion of the construction program including mechanical testing is scheduled for early fall, 1978.

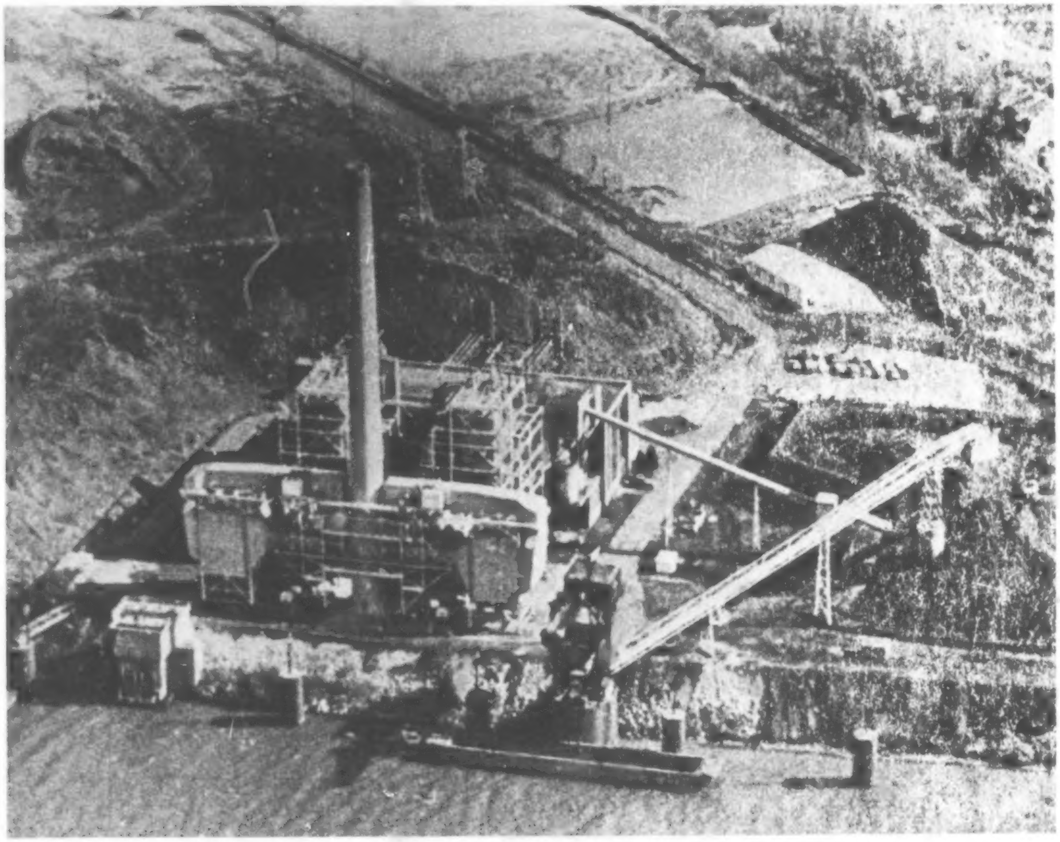
Phase III – Consists of plant startup and performance testing which will take place at the conclusion of Phase II. This Phase is expected to take three months.

Phase IV – A one year demonstration emission testing and performance evaluation program will be conducted by the Radian Corporation (Radian) of Austin, Texas who has been retained by the Bureau of Mines as an independent testing and evaluation contractor. Completion of the one year demonstration test is expected in late 1979 after which time, St. Joe fully expects to continue operation of the Demonstration Plant to achieve continued compliance with applicable environmental regulations.

## THE HOST SITE

To supply electric energy to its Monaca Zinc Smelter, in 1958 St. Joe completed construction of a 120 MWe steam electric power generating station consisting of two identical units. The G.F. Weaton Station is situated along the south bank of the Ohio River near Pittsburgh and is connected to the smelter electrical system by means of a 4,000 foot long high voltage transmission line transporting at 13,800 volts. The St. Joe power plant is essentially a base loaded station supplying approximately 95 percent of the total smelter electrical energy demand while operating at a 90 percent unit load factor on a continuous basis. Figure 1 shows an aeral view of the G.F. Weaton Power Station.

Figure 1 Aeral View of G. F. Weaton Station.



The plant is a conventional pulverized coal-burning steam generating electric utility utilizing the unit system; that is, a direct coupled boiler-turbine-generator arrangement. In addition to supplying the smelter electrical load, the G.F. Weaton Station is interconnected via a 25 MWe interchange with the local utility, Duquesne Light Company.

The power plant main steam flow is 450,000 lb/hr at 1000° F, 1850 PSIG with integral reheat steam of 334,000 lb/hr at 1000° F, 424 PSIG for each boiler at maximum load. The overall power plant heat rate is approximately 10,200 BTU/kWh. Boilers operate with five stages of feed water heating and utilize steam turbine drive boiler feed pumps. Each boiler has its own economizer, superheater, combustion air preheater, draft fans, and combustion control for independent operation.

Approximately 85,000 tons of coal is stockpiled adjacent to the power plant. Coal is transported by belt conveyor to coal bunkers atop the power station for pulverization. For the purpose of the Citrate Process Demonstration Plant, coal will contain sulfur ranging from 2.5 - 4.5 percent, with less than 15 percent ash and an HHV of approximately 12,500 BTU/lb. Bottom ash from each boiler and fly ash from the precipitators are conveyed to an ash settling pond for decantation and drying and subsequent disposal.[4]

Particle control is achieved through a combination mechanical and two-stage electrostatic precipitator which allows a combined particle removal efficiency which exceeds 99.6 percent. The power plant flue gases after leaving the particle collection equipment are discharged to the Citrate Process Demonstration Plant for desulfurization. The Demonstration Plant is sized to handle the peak load of one 60 MWe unit. After treatment in the Citrate Plant, the scrubbed gases are then exhausted to atmosphere through a stack mounted on the top of the absorption vessel. Cleaned flue gases are discharged to atmosphere at an elevation of two hundred feet above grade.

## CHEMISTRY AND PROCESS DESCRIPTION

As previously reported in Bureau of Mines and American Chemical Society publications, the absorption of $SO_2$ in aqueous solution is pH-dependent, increasing with higher pH. Because dissolution of $SO_2$ forms $H_2SO_3$ (sulfurous acid) with resultant decrease in pH, the absorption of $SO_2$ in aqueous solution is self-limiting. However, by incorporating a buffering agent in the solution to inhibit pH drop during $SO_2$ absorption, substantially higher $SO_2$ loadings can be attained. The principal function of citrate or other carboxylates is as the buffering agent during $SO_2$ absorption. Thiosulfate ion serves a major role in complexing absorbed $SO_2$ and thus inhibiting oxidation to sulfate. Hydrogen sulfide for the process may be made by reacting sulfur and steam with a reductant such as methane or carbon monoxide in a catalytic reactor. Regeneration of the absorbent solution by removing all $SO_2$ as elemental sulfur enables substantially complete $SO_2$ removal from gaseous emissions. The process chemistry is detailed and is outside the scope of this paper.

Information on Citrate Process chemistry has been previously reported and is cited in the references.[5,6]

As shown in the generalized process flowsheet, Figure 2, the Citrate FGD Process scrubber fits into the coal-fired power generating cycle between the fly-ash removal system and the stack. It should be noted that on new units significant capital savings in particle removal equipment can be realized by incorporation of the particle removal with the wet scrubbing and gas cooling unit operation associated with the Citrate Process. This savings potential was not realized in the St. Joe project due to retrofit considerations associated with the existing power plant.

The Demonstration Plant design utilizes a single process train consisting of gas cooling and $SO_2$ absorption, sulfur precipitation, sulfur recovery, sodium sulfate removal, and $H_2S$ generation unit operations. Flue gas ducting, steam supply, and utilities are arranged such that St. Joe's G.F. Weaton Unit No. 1 is tied directly to the Demonstration Plant. G.F. Weaton Unit No. 2, a physical twin of Unit No. 1, is also capable of supplying steam and utilities. The process is described as follows:

## Ash Removal, Gas Cooling, and $SO_2$ Absorption

Flue gas is transported to the Citrate Process Demonstration Plant by booster blowers. Ash removal and cooling of flue gas entering the process plant are accomplished simultaneously by contacting the gas with water in an eductor type venturi scrubber. The flue gas is cooled from 300° F to 120° F by both humidification and sensible cooling. High liquid recirculation rates are required for sensible cooling; the eductor design utilizes this high flow to reduce the fan requirements of the system. Transfer of $SO_2$ to the citrate solution in the absorber is more efficient at 120° F than it would be at adiabatic saturation of flue gas which is typically 128° F. All of the HCl and $SO_3$ in the flue gas are removed as hydrochloric and sulfur acids respectively in the venturi scrubber and $SO_2$ absorber.

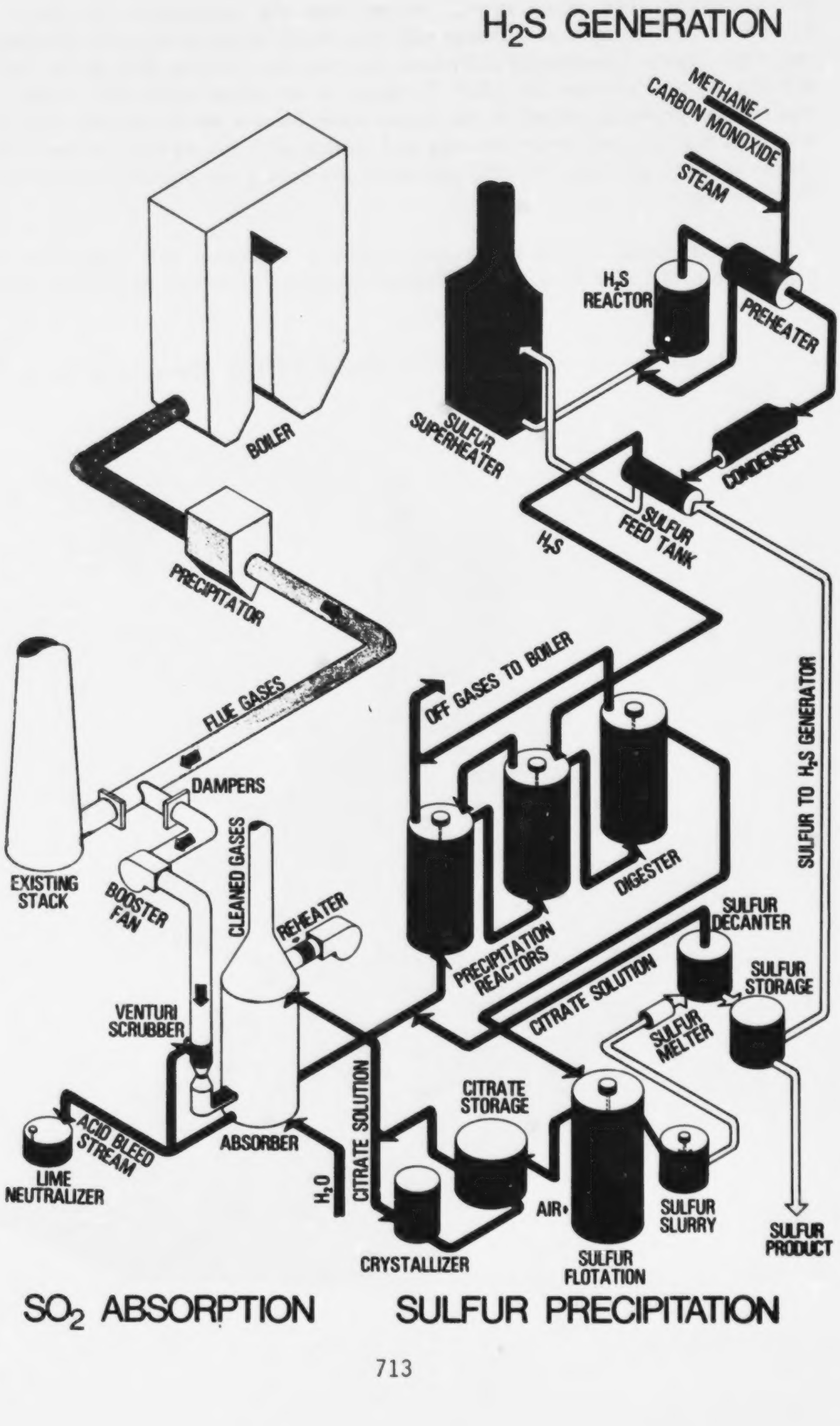
A bleed stream is taken from the venturi recycle steam to prevent build-up of ash and acids. This stream flows through a packed column countercurrent to a stream of air where $SO_2$ is stripped from the liquid and recycled to the scrubber. The stripped liquid is discharged to an agitated tank where it is neutralized with lime. From there it is pumped to the existing ash pond. The scrubber recycle stream is cooled from 120° F to 112° F by heat exchange with cooling water before entering the venturi. A makeup stream is added to the recycle to replace water lost by vaporization in the venturi and water removed in the bleed stream.

The cooled, cleaned flue gas then enters a packed absorber where it flows upward countercurrent to descending citrate solution. More than 90 percent of the $SO_2$ is removed from the flue gas by the following overall reaction which is enhanced by the buffering properties of the citrate solution:

$$SO_2 + H_2O \rightleftarrows HSO_3^- + H^+$$

When required by ambient conditions, the treated flue gas from the absorber is reheated by blending with steam heated air to aid dispersion and is discharged to atmosphere at a point 200 feet above grade via a stack mounted on top of the $SO_2$ absorber.

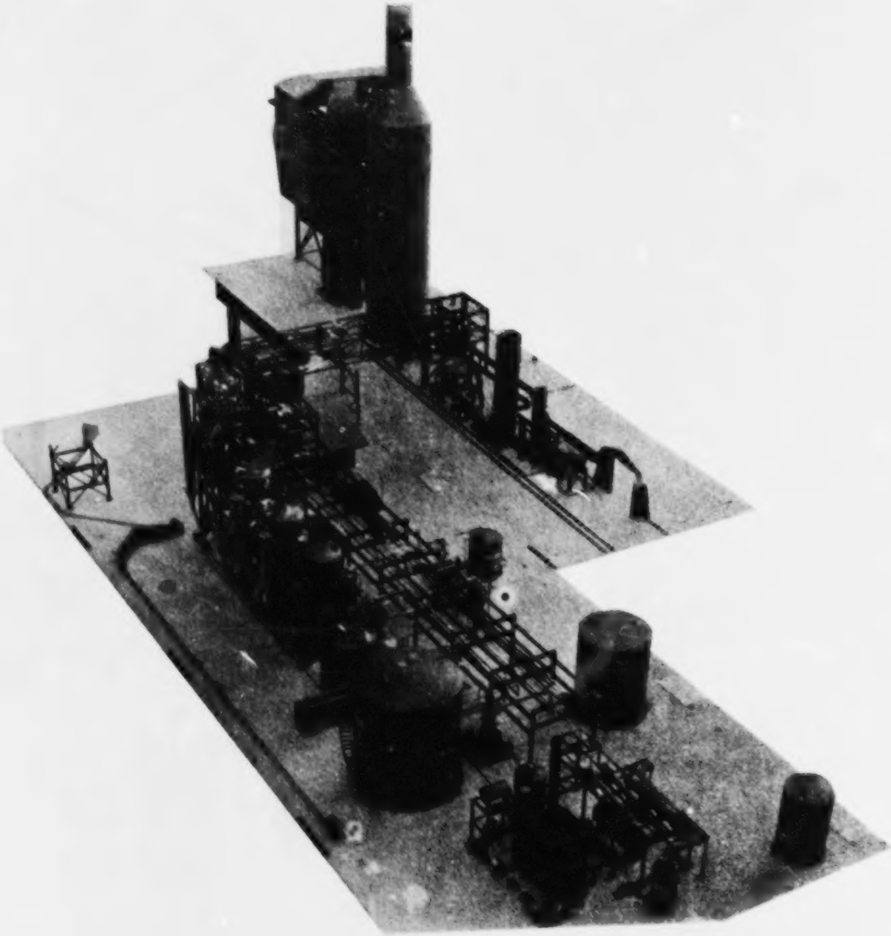
Figure 2 Generalized Process Flow Sheet.



Citrate solution leaving the absorber flows in series through two tandem reactors in the sulfur recover section. The citrate recycle stream from the regeneration section is cooled from 131° F to 123° F by heat exchange with river water before entering the absorber. Because of the three degrees temperature difference between the entering flue gas at 120° F and the entering citrate solution at 123° F, water is vaporized from the citrate stream. This vaporization provides control on the citrate water balance which includes water formed in the $SO_2/H_2S$ reaction and water entering and leaving with the various process streams such as caustic makeup, gas from the $H_2S$ generator, gas leaving the regeneration reactors, and citrate bleed streams.

Arrangement details of the gas cooling and $SO_2$ absorption unit operations are shown on Figure 3 in addition to the general arrangement of the Citrate Process Demonstration Plant.

Figure 3 Details of Gas Cooling and $SO_2$ Absorption Unit.



## Sulfur Precipitation and Recovery

Sulfur is formed by contacting the $SO_2$-rich solution with an $H_2S$-$CO_2$ gas from the hydrogen sulfide generating unit. The gas is sparged into the second of two reaction tanks each equipped with a turbine agitator which disperses the gas into the liquid. The $H_2S$ gas that is not reacted in the second reactor flows countercurrent into the first reactor which it is again dispersed into the liquor.

Off-gas which is mainly $CO_2$ with small quantities of $H_2S$, $CS_2$, and COS from the reactor system is sent to the boiler firebox for incineration via a surge drum. The reactors are stepped to provide countercurrent flow of gas and liquid. The $H_2S$ reacts according to the following equation:

$$HSO_3^- + H^+ + 2H_2S \rightarrow 3S + 3H_2O$$

Crystalline sulfur is formed in the reactors and sulfur slurry flows to a digester where a small stream of $SO_2$-rich solution from the absorber is reacted with any dissolved or entrained hydrogen sulfide in the slurry entering the digester. From the digester, the slurry flows to the sulfur flotation tank.

Separation of the sulfur from the bulk of the solution is accomplished by flotation with air. Sulfur froth, concentrated to about 10 percent solids, is separated from the top of the solution and flows to the sulfur slurry tank.

Regenerated citrate solution is drawn from the bottom of the flotation tank and returned to the absorber. The vapor spaces of all equipment downstream of the reactor system are tied into an exhaust system. An exhaust fan draws vapors containing traces of $H_2S$ and COS and discharges into the boiler firebox where these gases are incinerated. $SO_2$ generated from the combustion of these exhaust vapors is recycled to the Citrate Process Plant for desulfurization.

Sulfur is separated from the remaining solution by heating the slurry to about 260° F with steam in a shell and tube exchanger. The molten sulfur and the citrate solution are separated by gravity in a pressurized, steam-jacketed decanter vessel. The molten sulfur is discharged continuously from the bottom under interface level control and flows to a heated storage tank. The citrate solution leaves the top of the decanter and returns to the first reactor.

Two-thirds of the molten sulfur is pumped to the hydrogen sulfide generating unit as feedstock for the manufacture of $H_2S$ gas. A filter is provided to minimize the chance for any solids being pumped to the sulfur vaporizer in the $H_2S$ generator. The remaining one-third is product sulfur having a purity greater than 99.5 percent.

### Sulfate Removal

Up to one and one-half percent of the $SO_2$ entering the absorber forms sulfuric acid rather than sulfur by the following reaction:

$$HSO_3^- + H^+ + \tfrac{1}{2}O_2 \rightarrow H_2SO_4$$

In addition, the $SO_3$ that is not removed in the gas scrubbing section also forms sulfuric acid in the citrate solution. The sulfuric acid must be neutralized with caustic to form sodium sulfate by the following reaction:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

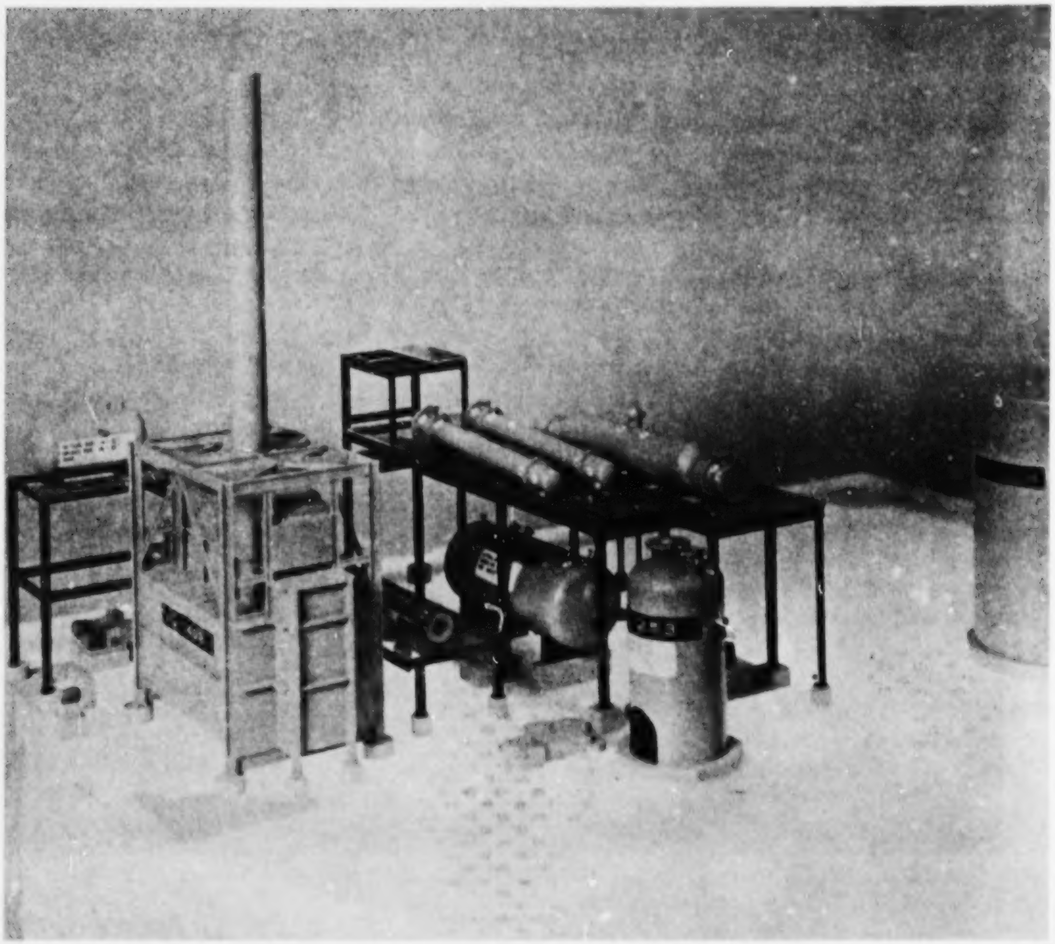
Sodium sulfate decahydrate is continuously removed from the citrate solution by vacuum crystallization. The sodium sulfate decahydrate (Glauber's Salt) crystals produced are subsequently recovered for disposal or use as a secondary feedstock in the chemical industry.

### Hydrogen Sulfide Generation

For demonstration purposes, on site generation of hydrogen sulfide gas is accomplished using recovered elemental sulfur, a gaseous reductant, and turbine extraction steam as consumptive feedstocks. $H_2S$ generation is based on the reaction of methane (natural gas), sulfur, and steam in a fixed-bed catalytic reactor, using a proprietary process developed by Home Oil Company Limited of Calgary, Alberta, Canada. The conversion efficiency of this reaction is greater than 95 percent and the impurities in the $H_2S$ product are mainly inert carbon dioxide and water vapor.[7,8]

Carbon monoxide, methanol, and propane reductants have all been successfully tested in the laboratory and operated briefly in a pilot plant test as substitutes for the methane feedstock. Utilization of carbon monoxide as an alternate feedstock is being incorporated in the Demonstration Plant design as an option should available supplies of methane be limited in the future.[8] Equipment layout of the $H_2S$ generator is shown in Figure 4.

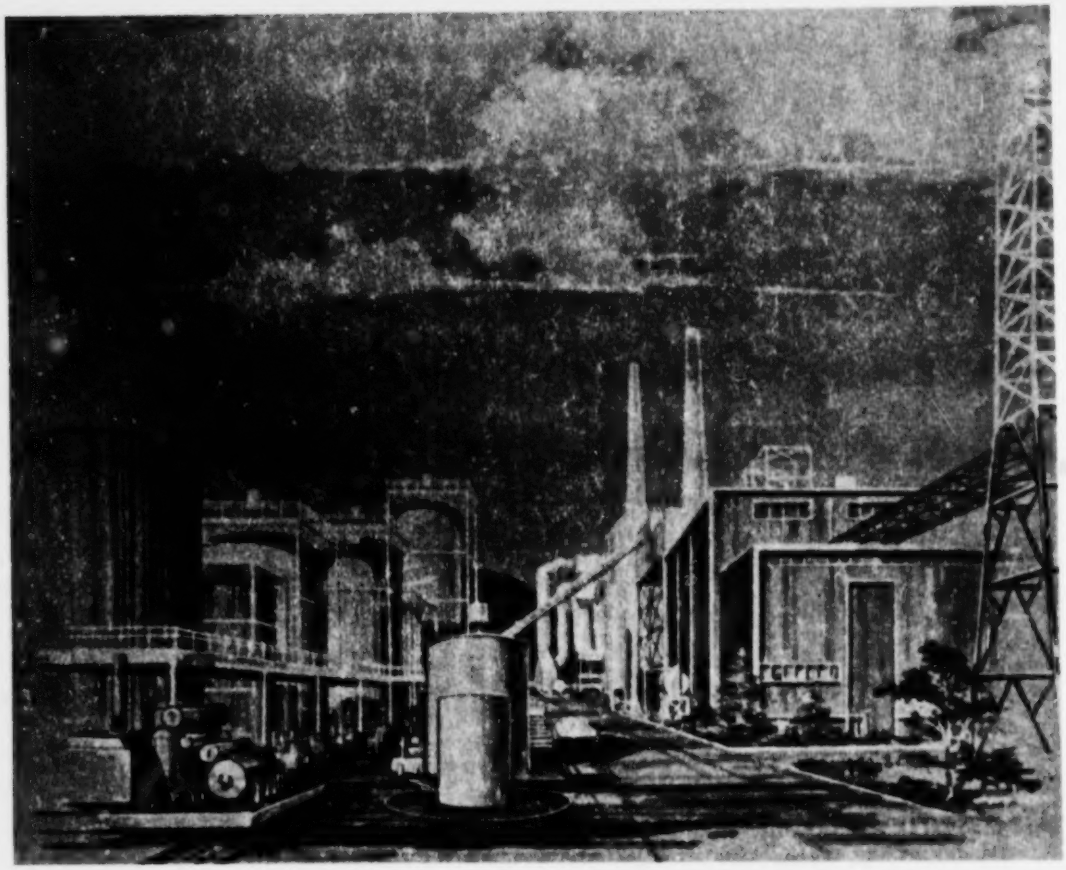
Figure 4 Equipment Layout of $H_2S$ Generator.



## THE DEMONSTRATION PLANT

Figure 5 is an artist's visulization of the completed Citrate Process Demonstration Plant as tied into the existing G.F. Weaton Power Station.

Figure 5   Artist's Conception of Plant.



## Design Features

The St. Joe Citrate Process Demonstration Plant engineering and design criteria incorporated a number of engineering features and considerations that will assure continuous plant operations, maximum performance with minimum downtime, and with minimum impact to power plant operations. Engineering features included in the final design which emphasize this philosophy follow.

- The system is designed to treat the flue gas equivalent to a nominal 60 MWe of electric generating capacity for a modern utility boiler having an overall heat rate of 10,200 BTU/kWh. The coal fired during the demonstration period will be of sulfur content ranging from 2.5 - 4.5 percent and an ash content not exceeding 15 percent.

- The system is designed to exceed the $SO_2$ and particulate removal requirements of the Federal New Source Performance Standards for coal-fired steam generators (1.20 lbs $SO_2/10^6$ BTU and 0.10 lbs particulate matter/$10^6$ BTU). In all cases, the system will remove at least 90 percent of incoming $SO_2$ for inlet concentrations above 2,000 PPM and will emit no more than 200 PPM (undiluted) for inlet conditions below 2,000 PPM. In addition, the plant will meet the Pennsylvania Air Quality Regulation of 0.695 lbs of $SO_2$ per $10^6$ BTU heat input to the boiler.

- The system will maximize the portion of recovered sulfur which leaves the process as elemental sulfur having a minimum assay of 99.5 percent and is suitable for use in a sulfur burning contact sulfuric acid plant.

- In the event of natural gas curtailments, the $H_2S$ generator is designed to operate on carbon monoxide as an alternate reducing gas. A plant gas containing approximately 68 percent CO is available from the adjoining smelter electrothermic zinc reduction furnaces.

- The Citrate Process Demonstration Plant can be tested to ultimate capacity. The existing flue ducting configuration allows for transfer of additional untreated flue gases from the adjoining twin boiler to the Citrate FGD unit without physical modification of gas ducting; flue gas transfer is achieved by balancing fan head and stack draft. Approximately 18 percent excess fan capacity is provided that will allow for gas treatment during overload conditions. Operation of the Demonstration Plant under ultimate conditions will allow for optimizing of the various process unit operations and will provide the design basis for future commercial applications.

- The Demonstration Plant design will permit operation with other absorption buffers in lieu of citrate such as glycolic or other similar organic acids. Also, reductants other than natural gas, e.g., carbon monoxide, can be used for the production of $H_2S$ gas.

- Flue gas from the power plant can be directed to either the Citrate FGD plant for $SO_2$ treatment or to the existing 275 foot stack for direct atmospheric discharge without interruption to power plant operations by control of the booster fan head. A series of flow sensors is provided in the flue ducting to determine the presence or absence of flue gas flow. Booster fan head is then automatically adjusted to respond to system flow requirements. In addition, provision has been made in the plant design to permit physical isolation of the FGD system from the power plant.

- Gravity drainage is provided for citrate liquor lines to a common citrate storage tank; thereby, in the event of a power failure or other unscheduled outage under winter conditions, a pipeline freeze-up would be prevented. Additionally, the entire system is "winterized" to prevent standby equipment failure.

- The Demonstration Plant is designed to avoid the possibility of a power plant "trip-out."

- Redundancy of critical mechanical and process components is provided throughout the plant. All process pumping systems have 100 percent built-in standby capacity. Critical control valves are provided with manual overrides and/or inline by-passes. The configuration of sulfur precipitation reactors and agitators is such that total bypass of a reactor is possible without process shutdown.

- An emergency quench system is provided in the event of high temperature flue gas excursions which would otherwise damage the absorber polyester lining and associated polypropylene lined pipe. In the event of a boiler air preheater drive mechanism failure, feed gas temperatures could rise to 600° F. This has been considered in the design of the flue gas booster fan and the venturi quench. The booster fan is provided with a "cool-down" motor to preclude impellor blade warping.

- The precipitation of sulfur within $H_2S$ transport lines, reactor vessels, and sparger assemblies is a recognized problem area and is prevented through the use of a proprietary method.

- Cleaned flue gas can be reheated either by mixing with steam heated air or by an alternate direct combustion fuel oil reheater.

- To preclude accelerated corrosion and premature failure of the $H_2S$ generator, design provisions are included for equipment preheat and warm "coasting operation" during periods of power plant outage or Citrate Plant shutdown.

- Plant operability was thoroughly considered in the plant design. Features such as semi-graphic display panels, local and remote control for vital services, repetition of key instrumentation at the power plant control room for critical operational areas such as $H_2S$ ambient sensing and high gas temperature excursions are provided.

- Recognizing that the power plant must be capable of rapid load fluctuations, the plant turndown is designed to 60 percent with process adjustments capable of being made at either the control panel or locally.

- A flare system is provided for incineration of unconsumed $H_2S$ product during plant startup/shutdown and transient plant operations.

- A common sump system is provided to collect all surface drainage including inadvertent chemical spills. The sump water is monitored and pumped to disposal only when safe.

## Mechanical and Process Equipment

Equipment selection was made on a scale that approximates one train of a full scale, multi-train commercial installation. The items of equipment used in the process are capable of being scaled up (or down) so that once demonstrated in the plant, the process can be applied with confidence to larger (or smaller) coal-burning boilers. Wherever possible, the type of equipment selected for the Demonstration Plant has had a successful history of commercial operation in similar applications.[9]

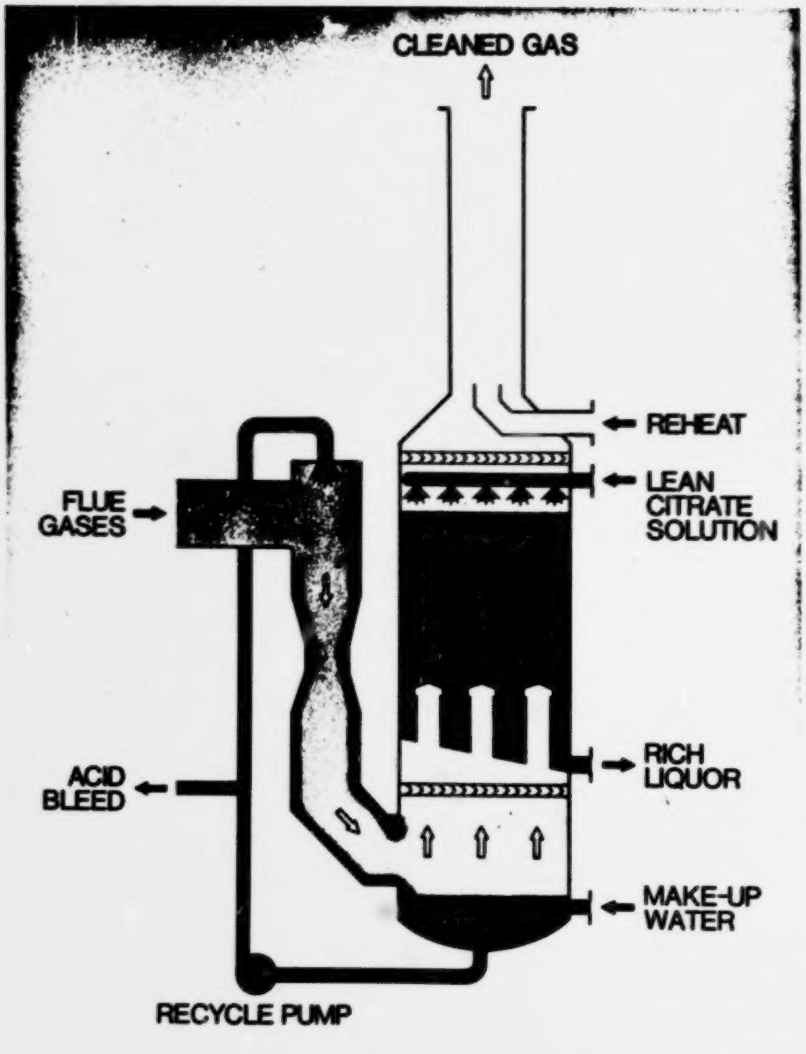
Materials selection was based on protection of all process wetted surfaces from general corrosion associated with the sodium citrate liquor and chlorides derived from the wet scrubbing of combustion flue gases. The materials selected are economic choices and are typical of those that would be used in future large scale operating plants. A description of the principal major equipment and process unit operations follows.

## Columns, Vessels, and Tanks

SO2 Absorber. One required. 26'-0" I.D. x 85'-0" high, material-carbon steel, flake glass lined. 120" I.D. inlet duct. Two chevron separator elements in chlorinated PVC. 20'-0" bed of size 2 polypropylene Intalox saddles. Liquid distributor and support plate in flake glass lined carbon steel. One chimney tray having 4 each 6'-6" dia. chimneys and vortex breaker for liquid draw off. Gas discharge stack 10'-0" I.D. x 102' high mounted on top of absorber.

Venturi Scrubber. One required. Gas rate – 156,000 SCFM at 120° F, 14.7 PSIA liq. rate – 4500 GPM at 40 PSI at nozzle. Materials – venturi nozzle of Inconel-625, body of carbon steel, acid proof brick lined over rubber membrane. 120" dia. x 45' high.

Figure 6 $SO_2$ Absorber/Venturi Scrubber.



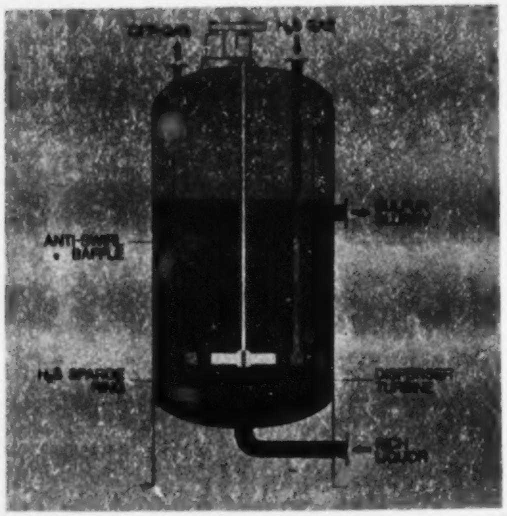
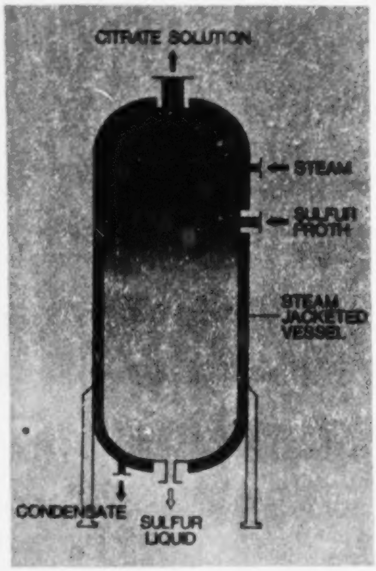


Figure 7 Sulfur Precipitation Reactor.

Sulfur Precipitation Reactors. Two required. 12'-10" I.D. x 18'-10" TT material carbon steel with 1/8" corrosion allowance, flake glass lined with Inconel-625 trim. Staggered elevation of each by 19' – fitted with top mounted disperser turbines rated at 100 HP and tip speed approx. 1000 FPM. Operating pressure 10 PSIG at 131° F; liquid capacity 13,000 Gal.

Sulfur Decanter. One required. Hastelloy C-276 clad carbon steel, cladding 1/8" thick; steam jacketed. Operating pressure 65 PSIG at 260° F.

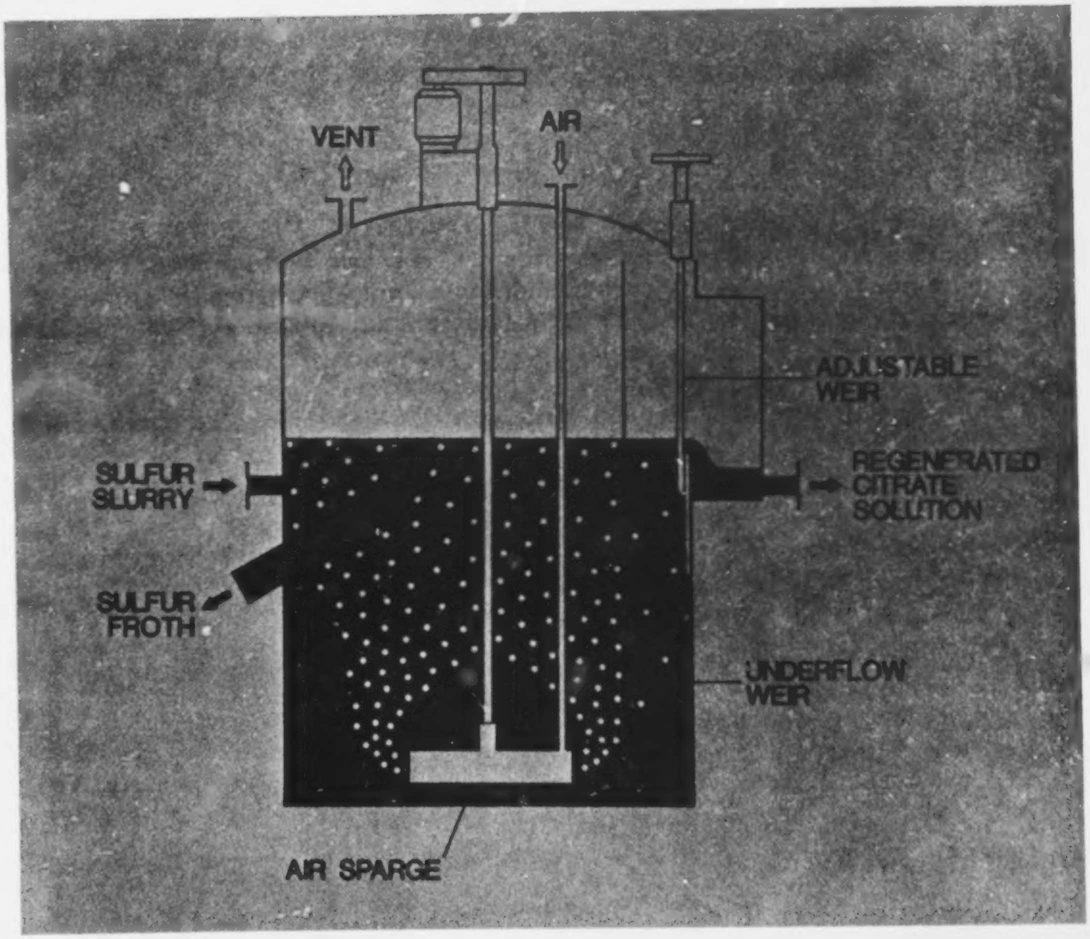
Figure 8 Sulfur Decanter.



Digester. One required. 12'-0" I.D. x 18'-0" TT. Material carbon steel, flake glass lined. With top mounted Inconel-625 agitator.

Sulfur Flotation Tank. One required. Cylindrical vessel 15'-0" I.D. x 20'-0" high; 18,500 Gal. capacity; carbon steel; flake glass lined. Fitted with Inconel-625 turboagitator.

Figure 9 Sulfur Flotation Tank.



Sulfur Slurry Tank. One required. 15'-0" I.D. x 15'-0" high, carbon steel, flake glass lined. Fitted with top mounted Inconel agitator. Operating pressure – atmospheric at 131° F. Max. filling rate – 130 GPM.

Citrate Solution Storage Tank. One required. 28' I.D. x 30' high, carbon steel, flake glass lined. Fitted with side mounted Inconel-625 agitator.

Make-up Tank. One required. 5'-0" I.D. x 7'-6" high, reinforced fiberglass construction. Installed in ground. Fitted with a pump and agitator.

Sulfur Storage Tank. One required. 20'-0" I.D. x 24'-0" high, capacity 56,000 Gal., carbon steel. Equipped with external plate steam coils and insulation.

Heat Exchangers and Heaters

Venturi Wash Water Cooler. One required. Duty 19.8 $10^6$ BTU/hr. Plates – Palladium stabalized titanium, 96 PSIG operating pressure.

Lean Solution Cooler. One required. Duty 5.4 $10^6$ BTU/hr. Plate type – Palladium stabalized titanium; operating pressure 78 PSIG at 131° F.

Sulfur Melter. Two required. Duty – 4.11 $10^6$ BTU/hr. Jacketed pipe type: Tubes – Hastelloy C-276. Shell – carbon steel 35 PSIG steam operating. Sulfur slurry temperature IN-131° F; OUT-260° F.

Pumps

Sulfur Slurry Pump. Two required. Rotary type, 64 GPM, 105 PSI pressure differential, pumping temperature 131° F. Rubber lined Hastelloy-C with Hastelloy-C rotor and trim, variable speed belt drive 20 HP electric motor.

Make-up Pump. One required. Vertical centrifugal type 100 GPM, 27 PSI pressure differential-pumping temperature 111° F; Hastelloy-C case, impellor and trim, direct coupled 5 HP electric motor.

Sulfur Transfer Pump. One required. Centrifugal, horizontal single stage type, steam jacketed, 15 GPM, pumping temperature 260° F, 72 PSI pressure differential case and Impellor of cast steel with direct drive 7.5 HP electric motor.

Sulfur Loading Pump. One required. Centrifugal, horizontal single stage type, steam jacketed, 50 GPM, pumping temperature 260° F, 20 PSI pressure differential case and Impellor of cast steel with direct drive 3 HP electric motor.

Scrubber Recycle Pump. Four required. Horizontal centrifugal slurry type; two pump tandem installation, 4500 GPM, 118 PSI pressure differential, pumping temperature 120° F; rubber lined cast iron case and Impellor with Hastelloy-C trim, 250 HP electric motor with belt drive.

Rich Citrate Solution Pump. Two required. Centrifugal, horizontal single stage type, pumping temperature 120° F. Chlorimet 3 case and impellor with Hastelloy-C trim; 40 HP electric motor drive.

Lean Solution Pump. Two required. Centrifugal, horizontal single stage type, pumping temperature 121° F, Chlorimet 3 case and impellor with Hastelloy-C trim, 120 HP electric motor drive.

Blowers and Agitators

Flotation Air Blower. Two required. Lobe type, 9 PSI pressure differential, carbon steel construction.

Flue Gas Fan. One required. Double inlet mechanical draft type. 234,000 ACFM normal (275,000 ACFM peak), discharge pressure 9.7 "$H_2O$ W.C. (normal) 13.4 "$H_2O$ W.C. (peak) at 300° F; carbon steel construction; direct coupled 1000 HP electric motor; provided with auxiliary "cool-down" motor.

Other Major Equipment

$H_2S$ Generator. One required. 825 SCFM of approximately 80 percent $H_2S$ gas at 45 PSIG and 300° F. Material – stainless steel shells lined with high temperature refractory. Proprietary design.

## Operational and Performance Parameters

The Citrate Process Demonstration Plant is designed for a high level of performance with a minimum of operational constraints. Citrate Process performance and operational parameters are best described by the inherent characteristics of the process which provides for a high surge capacity, simple direct regeneration, no scaling or plugging in the absorber, insensitivity to $CO_2$ and $O_2$, ability to abate $SO_2$ in a wide range of flue gas concentrations, a non-hazardous biodegradable absorption media, low residual $SO_2$ (below 200 PPM), elemental sulfur product, low consumption of energy, and no solids disposal problems.

These characteristics contribute to the simplicity, reliability, and economy of the Citrate Process. Specific operational and performance parameters of the Citrate Process as applied to the St. Joe project can be seen on Table 1.

Table 1 OPERATING PERFORMANCE PARAMETERS

| Parameter | Units | Operating Range |
|---|---|---|
| Flue Gas Rate | SCFM | 156,000 |
| Cooled Flue Gas Temperature, Contact | °F | 120 |
| $SO_2$ Loading | | |
| at Inlet | PPM | 2,000 |
| at Outlet | PPM | 200 |
| $SO_2$ Removal Efficiency | % | 90 |
| Sulfur Recovered From Flue Gas | TPD | 15.5 |
| Sulfur Product Purity, Min. | Wt. % | 99.5 |
| Particulate Loading | | |
| at Outlet | gr/SCF | trace |
| Excess Combustion Air | % | 15 |
| Boiler Fuel, as received | | |
| Sulfur Content, weight | Wt. % | 2.5-4.5 |
| HHV | BTU/lb | 12,500 |
| Ash Content, weight | Wt. % | 11.5 |
| Chlorides | Wt. % | 0.2 |
| Utility Requirements | | |
| Steam | lb/hr | 10,900 |
| Electric Power, max. | kWh | 1,600 |
| Cooling Water, average | GPM | 2,600 |
| Fuel Oil No. 2, superheater | lb/hr | 188 |
| Personnel Requirement | | |
| Operations | MH/day | 56 |
| Maintenance | MH/yr | 6,420 |
| Plant Turndown | % | 60 |
| Number of Process Trains | Each | 1 |
| Absorber $\Delta$ P | "$H_2O$ | 6 |
| Absorber L/G | GPM/1000 SCF | 7.7 |
| Eductor Venturi L/G | GPM/1000 SCF | 28.8 |
| Citrate Solution pH | pH | 4.5 |
| Reactor Residence Time, each | Min. | 10 |
| Oxidation to Sulfate | % | 1.5 |
| Chemical Feedstock Requirement | | |
| Citric Acid | lb/ton sulfur recovered | 28.7 |
| Caustic Soda | lb/ton sulfur recovered | 92.0 |
| Methane* | SCFM | 168 |
| Carbon Monoxide, 68% purity* | SCFM | 868 |
| Sodium Thiosulfate | lb/hr | 6.2 |
| Lime (neutralization) | lb/hr | 145 |

*Alternate process feedstock.

## ONE YEAR DEMONSTRATION TEST PROGRAM

Following the completion of plant performance testing and final acceptances, a one year demonstration test will be initiated. The objectives of the demonstration test are:[10]

- To characterize completely the citrate system with respect to the various system operating parameters.
- To determine the system's optimum operating conditions.
- To determine long-term system reliability.
- To determine the environmental impact of the citrate system.
- To determine the technical and economic feasibility of the citrate system.
- To document the results of the test program such that comparisons of the citrate system with other flue gas desulfurization systems can be performed.

To insure that the Demonstration Test Program objectives are fulfilled, the Bureau of Mines has retained the Radian Corporation (Radian) to serve as an independent, unbiased test and evaluation contractor.

To accomplish these objectives, Radian will develop and implement a test plan which includes:

- Baseline testing which will be divided into two distinct segments. One segment will observe actual boiler operation over a period of about four weeks, while monitoring all available boiler operating parameters and effluent discharges. The second segment of the baseline testing will investigate the historical limits of transient boiler operation. This segment will be executed during the three- to four-week testing period. The coordination of these two segments will ensure that the boiler is operating at historically normal conditions during the test period.

- Acceptance testing which will be performed to certify that the Citrate Process Demonstration Plant will meet performance guarantees. The acceptance test will require the system to operate for a period of not less than ten (10) consecutive days while burning coal containing not less than 2.5 percent sulfur and meeting both the New Source Performance Standards and a 90 percent $SO_2$ removal efficiency.

- Optimization of the system will be investigated through the one-year demonstration period. Data collected during the demonstration testing will be used to determine what adjustments are required to optimize plant operations to minimize absorber liquid/gas ratio, system pressure drop, reagent and feedstock consumption, power and utility consumption, and process costs and to maximize $SO_x$ removal, particle removal, system reliability, and system availability.

- Documentation of the citrate system's performance which will include reliability, availability, and utilization information. For proper overall power station operation, FGD system availability should be maintained at high levels. Information concerning boiler and citrate system operation will be gathered daily and reported monthly. System performance will be reported in terms of availability, reliability, and utilization. Availability is defined as the percentage of a given time period that the FGD system is available for operation. Reliability is the percentage of instances that the FGD system operated when it was called upon to operate. Utilization, a third performance parameter, will also be reported. Utilization is the percentage of time that the boiler operated during a time period and reflects the load demand imposed on the FGD system.

Special studies to investigate sulfate formation, system corrosion, materials evaluation, stack gas reheat, and other items of interest will also be conducted during this one year period. In addition, process economics will be developed based upon the demonstration project information.

Successful completion of this project will provide information for economic and technical comparison of the Citrate Process and other FGD systems. This information will be gathered during commercial scale operation and will be useful for extending G.F. Weaton experience to other systems.

## ENVIRONMENTAL AND ENERGY IMPACT

The products of the Citrate Process are high purity elemental sulfur and an industrial grade of Glauber's Salt (sodium sulfate slurry). Process energy demand in terms of electric power, steam, and methane/carbon monoxide are low compared to other $SO_2$ abatement processes.

### Environmental Impact

As required by the National Environmental Policy Act of 1969, the Bureau of Mines[11] identified the disposition of the following product and waste streams associated with the St. Joe Citrate Process Demonstration Plant:

- Treated flue gas, 156,000 SCFM. Flue gas will be discharged to the atmosphere and will contain approximately 0.02 volume percent (200 ppmv) $SO_2$.

- Product sulfur, 15 tons per day, either as a solid or liquid product sulfur will be of a commercially pure grade and will be used by St. Joe to produce sulfuric acid at its nearby zinc smelter.

- Cooling and condensate water streams. Water streams that are not recycled will be discharged in an environmentally acceptable manner.

- $H_2S$ gas during startup or transient conditions. This gas will be incinerated to $SO_2$. The maximum $SO_2$ emission to the atmosphere during startup will be 3,300 pounds $SO_2$ per hour for 30 minutes or a total emission of 1,650 pounds of $SO_2$. The maximum $SO_2$ emission to the atmosphere during upset conditions will be 6,600 pounds of $SO_2$ per hour for 10 minutes or a total emission of 1,100 pounds $SO_2$. During the demonstration year of operation, two startup periods are expected. Upset conditions are estimated to take place no more than once a week and such conditions are expected to be of short duration. The emissions resulting from startup or transient conditions will be eliminated or minimized as experience is gained in operating and effectively using the installed instrumentation for process operation and control.

- Spilled citrate solution. A spillage collection system is provided to contain spilled solutions at a central point where they will be treated for recycling back into the process.

- Byproduct Glauber's Salt (sodium sulfate decahydrate), 5 tons per day, as a wet cake. Markets for the disposal of this byproduct have been surveyed and an offer to remove this byproduct for the end use of sodium sulfate has been received. The Glauber's Salt byproduct also may be sold to the paper industry.

- Gas prescrubber bleed waste stream, 72 tons per day, containing about 1½ tons fly ash. This stream will be neutralized with lime. The neutralized sludge, containing about one ton $CaCl_2$ and 1½ tons $CaSO_4$ per day, will join the power station's fly ash disposal stream which contains about 120 tons fly ash per day. The fly ash stream is ponded for solids settling.

- Sulfur precipitation reactor vent gases consisting mainly of $CO_2$ and trace $H_2S$ will be piped directly to the power station boiler for incineration of the $H_2S$ to $SO_2$ for recycle to the citrate scrubber.

- Combustion gases from the sulfur superheater. The superheater is fired with No. 2 fuel oil containing approximately 0.3 percent sulfur. The combustion gases will be discharged into the atmosphere after waste heat recovery.

- Vent gas from the flotation tank, sulfur slurry tank, and citrate storage tank. These vent gases may contain 100 ppm of COS and 10 PPM $H_2S$. The gas will be piped directly to the power station boiler for incineration of the COS and $H_2S$ to $SO_2$ for recycle to the citrate scrubber.

- Sulfur filter cake, 4.3 cubic feet every 12 days. This filter cake will contain mainly solid sulfur, diatomaceous earth with minor amounts of citrate salts and fly ash. The filter cake will be disposed of in an environmentally acceptable manner.

## Energy Impact

During a typical year of plant operations, as shown on Table 2, not more than 3.8 percent of the gross heat energy consumed by the St. Joe G.F. Weaton Power Station for either unit would be consumed for the benefit of the Citrate Process Demonstration Plant. Basis assumptions in the energy analysis are as follows:

- Coal fuel as received, HHV 12,500 BTU/lb.
- Flue gas reheat is used only as required to aid dispersion.
- Steam generation efficiency of the boiler is 88 percent.
- Power plant heat rate is 10,200 BTU/kWh.
- Waste heat energy is recovered where economically justified.
- Plant is assumed to be operating at full load with 95 percent availability.

Table 2 ENERGY IMPACT

| Energy Consumed | Energy Lost, BTU/yr |
|---|---|
| Energy used as Electric Power<br>(11.960 x $10^6$ kWh/yr) (10,200 BTU/kWh) | 12.22 x $10^{10}$ |
| Turbine Extraction Steam used for Reheat Flue Gas<br>(1.204 x $10^6$ lbs/yr of 476 PSIG steam)<br>(10,200 ÷ 7.23 BTU/lb) | 0.17 x $10^{10}$ |
| Reduction Steam for Process and Utility Service<br>(89.394 x $10^6$ lbs/yr of 125 PSIG steam)<br>(968 ÷ 88% BTU/lb) | 8.82 x $10^{10}$ |
| Subtotal | 21.21 x $10^{10}$ |
| Energy Saved | |
| Credit From Waste Heat Recovery<br>(8.41 x $10^9$ BTU/yr ÷ 88%) | 0.96 x $10^{10}$ |
| Net Energy Consumed, BTU/yr | 20.25 x $10^{10}$ |
| Power Plant Gross Energy Production | 536.00 x $10^{10}$ BTU/yr/unit |
| Citrate Process Energy Useage | 3.8% of gross energy produced from the combustion of coal in a single boiler unit. |

## CAPITAL AND OPERATIONAL COST

Functionally, the process flowsheet for both the 500 and 1000 MWe coal-fired power plant applications is the same as for the St. Joe Citrate Process Demonstration Plant. However, the number of process trains and physical arrangement of unit operations must be adjusted to reflect commercially available equipment and practical size limitations of specific process and mechanical components. The number of parallel components required for scaling up unit operations will vary to a certain degree depending upon the operational requirements of specific plants.

Capital and operational cost projections for application of the Citrate FGD Process to 500 and 1000 MWe utility boilers were prepared based on actual cost data derived from the Citrate Process Demonstration Plant definitive cost estimates. For the purpose of the cost projections shown in this paper, 1977 dollars are used in the capital cost estimate and 1978 dollars are used in the operational cost estimate.

Table 3 shows the capital cost for a 500 MWe FGD (coal-fired 2.5 percent) application using the Citrate Process to be $38,147,000 ($76/kW); for the 1000 MWe power plant, capital cost is $72,888,000 ($73/kW). Only a slight reduction in cost per kW was realized in going from 500 to 1000 MWe because practical size limitation for most process components have been reached on the 500 MWe plant. $SO_2$ removal cost using the Citrate Process on a levelized net expenses basis is shown in Table 4 to be 2.07 and 1.97 Mills/kWh for the 500 and 1000 MWe power plants, respectively. Levelized net expense is based on a ten year projection of net expense discounted at 10 percent per annum to the present. Net operational expense considers the direct and indirect expenses associated with the FGD plant operations and includes a credit for recovered sulfur product. Annualized operational cost expressed as Net Expense includes the net operational expense plus capital charges and applicable taxes.

Cost projections assumed a new power plant application in a midwest location burning a 2.5 percent sulfur coal. Cost projections do not show cost of land, access rights, or the cost of bulk particle removal. Residual particle removal, engineering and design services, construction management, material and labor cost and overhead, general and administrative expense, and contractor's fees are included.

Table 3 CAPITAL COST FOR A 500 MWe FGD APPLICATION

## CITRATE FGD PROCESS

### CAPITAL COST SUMMARY

### Coal Fired Power Plant - 2.5% Sulfur

| | 500 MWe | 1000 MWe |
|---|---|---|
| | —— $1,000 —— | |
| **DIRECT CONSTRUCTION COST** | | |
| MAJOR EQUIPMENT - BY UNIT OPERATION | | |
| I - GAS COOLING AND $SO_2$ ABSORPTION | 12,594 | 25,145 |
| II - SULFUR PRECIPITATION | 906 | 1,848 |
| III - SULFUR RECOVERY | 1,591 | 2,976 |
| IV - SODIUM SULFATE REMOVAL | 302 | 402 |
| V - $H_2S$ GENERATOR | 1,421 | 2,731 |
| VI - OFFSITES AND FACILITIES | 140 | 231 |
| SUBTOTAL | 16,963 | 33,333 |
| FOUNDATIONS AND CONCRETE WORK | 1,239 | 2,389 |
| STRUCTURAL STEEL | 860 | 1,649 |
| BUILDINGS | 100 | 110 |
| INSULATION | 667 | 1,171 |
| INSTRUMENTATION | 824 | 1,462 |
| ELECTRICAL | 828 | 1,482 |
| PIPING | 5,145 | 9,437 |
| PAINTING | 133 | 253 |
| MISCELLANEOUS | 567 | 927 |
| SUBTOTAL | 10,363 | 18,880 |
| TOTAL DIRECT CONSTRUCTION COST | 27,326 | 52,213 |
| INDIRECT COST AND FEE | 10,821 | 20,675 |
| TOTAL CAPITAL COST | 38,147 | 72,888 |
| COST/KW | 76 | 73 |

**BASIS**

NEW POWER PLANT APPLICATION - MIDWEST LOCATION.

INDIRECT COST INCLUDES ENGINEERING DESIGN, CONSTRUCTION OVERHEAD, TAXES, GENERAL AND ADMINISTRATIVE EXPENSE.

1977 DOLLARS.

Table 4 $SO_2$ REMOVAL COST USING CITRATE PROCESS

## CITRATE FGD PROCESS

### ANNUALIZED OPERATIONAL COST SUMMARY
### Coal Fired Power Plant - 2.5% Sulfur

| | | 500 MWe | | 1000 MWe | |
|---|---|---|---|---|---|
| | | 1ST. YEAR | 5TH. YEAR ** | 1ST. YEAR | 5TH. YEAR** |
| | | ($1,000) | | | |
| DIRECT OPERATIONAL EXPENSE | | | | | |
| CHEMICAL FEEDSTOCKS | | 1,789 | 2,762 | 3,584 | 5,464 |
| UTILITIES | | 4,461 | 6,717 | 8,923 | 13,434 |
| PLANT OPERATIONS | | 240 | 329 | 313 | 429 |
| PLANT MAINTENANCE | | 288 | 407 | 424 | 601 |
| PAYROLL OVERHEAD | | 129 | 175 | 169 | 230 |
| SUBTOTAL DIRECT | | 6,907 | 10,390 | 13,413 | 20,158 |
| INDIRECT EXPENSE | | | | | |
| ADMINISTRATIVE & OVERHEAD | | 208 | 273 | 208 | 273 |
| INSURANCE | | 308 | 374 | 589 | 682 |
| SUBTOTAL INDIRECT | | 516 | 647 | 797 | 955 |
| START-UP COSTS* | | 902 | 0 | 1,702 | 0 |
| TOTAL OPERATIONAL EXPENSE | | 8,325 | 11,037 | 15,912 | 21,113 |
| SULFUR PRODUCT CREDIT | | (1,258) | (1,529) | (2,517) | (2,917) |
| COST | NET OPERATIONAL EXPENSE | $7,067.00 | $9,508.00 | $13,395.00 | $18,199.00 |
| COST/TON COAL | | 5.90 | 7.94 | 5.59 | 7.59 |
| MILLS/KWH | | 2.12 | 2.86 | 2.01 | 2.73 |
| INTEREST | | 3,906 | 3,906 | 7,464 | 7,464 |
| DEPRECIATION | | 1,371 | 1,371 | 2,619 | 2,619 |
| TOTAL EXPENSE | | 12,344 | 14,785 | 23,478 | 28,282 |
| TAX BENEFIT | | (5,925) | (7,096) | (11,269) | (13,575) |
| ITC AT 10%* | | (1,539) | 0 | (3,019) | 0 |
| COST | NET EXPENSE | $4,880.00 | $7,689.00 | $9,190.00 | $14,707.00 |
| COST/TON COAL | | 4.07 | 6.42 | 3.83 | 6.14 |
| MILS/KWH | | 1.47 | 2.31 | 1.38 | 2.21 |
| COST/TON COAL | NET EXPENSE LEVELIZED *** | 5.76 | | 5.49 | |
| MILLS/KWH | | 2.07 | | 1.97 | |

BASIS

95% PLANT AVAILABILITY; 80% AVERAGE UNIT LOAD.
SULFUR CREDIT - $40/TON.
MAINTENANCE SERVICES FROM A FULLY STAFFED POWER PLANT MAINTENANCE ORGANIZATION.
(9.5% NONEXEMPT BONDS) SL DEPRECIATION - 25 YEARS.
UTILITY FINANCING METHOD EXPRESSED IN 1978 DOLLARS.
*FIRST YEAR ONLY.
**INCLUDES EFFECT OF MATERIAL, LABOR AND UTILITY ESCALATION.
***LEVELIZED OVER A 10 YEAR PERIOD AT 10% DCF.

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# APPENDIX

## Conversion Factors – Customary and SI Metric Units

| Unit | SI Unit |
|---|---|
| 1 inch | 2.5400 x $10^{-5}$ meter |
| 1 foot | 3.0480 x $10^{-1}$ meter |
| 1 U.S. gallon | 3.7854 x $10^{-3}$ $\text{meter}^3$ |
| 1 pound | 4.5359 x $10^{-1}$ kilogram |
| 1 ton | 1.0161 x $10^{3}$ kilogram |
| 1 $\text{lbs/in}^2$ | 6.8948 x $10^{3}$ $\text{newton/meter}^2$ |
| 1 BTU | 1.0551 x $10^{3}$ joule |
| 1 BTU/gal | 2.3208 x $10^{5}$ $\text{joule/meter}^3$ |
| 1 BTU/lb | 2.3260 x $10^{3}$ joule/kilogram |
| 1 hp | 745.700 watt |
| 1 kWh | 3.6 mega joule |
| 1 MWe | 1 megawatt |
| 1 SCFM | 4.72 x $10^{-4}$ SD $\text{meter}^3$/sec. |
| 1 grain | 0.065 grams |

# PHILADELPHIA ELECTRIC'S EXPERIENCE WITH MAGNESIUM OXIDE SCRUBBING

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## ABSTRACT

The particulate and sulfur dioxide removal system at Philadelphia Electric's Eddystone Station has undergone preliminary performance testing for the past six months. Particulate removal efficiencies in the range of 97-98 percent have been demonstrated on the fly ash escaping collection in the upstream, and 93 percent efficient mechanical-electrostatic precipitator particulate removal system. The MgO-based regenerative $SO_2$ scrubbing system has been operated at $SO_2$ removal efficiencies exceeding 95 percent. Salable 98 percent sulfuric acid has been produced from the scrubbed $SO_2$ and the regenerated MgO reused in the process.

A number of operating difficulties uncovered during this preliminary test period is described. The cumulative availability of 32 percent for the $SO_2$ scrubbing system with the longest continuous run being 140 hours has been disappointing.

Plans for future operation of the system are discussed.

# PHILADELPHIA ELECTRIC'S EXPERIENCE WITH MAGNESIUM OXIDE SCRUBBING

Philadelphia Electric Company embarked on a program to install a particulate and sulfur dioxide scrubber system at Eddystone Station in mid-1971. This paper reviews briefly operating experience with particulate and sulfur dioxide scrubbing, problems encountered, process economics, and schedule for completion of the system test program.

## SYSTEM AND PROCESS DESCRIPTION

The scrubber plant at Eddystone Unit 1 consists of three parallel scrubbing trains with a particulate scrubber, reheater and scrubber booster fan in each train. One train incorporates the $SO_2$ scrubber in series with the particulate scrubber (Figure 1). Two of the particulate scrubbers are Environeering Ventri-Rod units while the third is a Peabody-Lurgi Venturi unit. The $SO_2$ scrubber is also an Environeering Ventri-Rod unit equipped with two scrubbing stages and two stages of mist elimination (Figure 2). Flexibility of operation is incorporated in the ductwork through systems that permit by-passing the $SO_2$ scrubber, each train, or the entire scrubber plant.

The particulate and $SO_2$ scrubbers have separate surge tanks for slurry collection, pH control and make-up (Figure 3). These surge tanks are fabricated from carbon steel with a polyurethane lining, as is the $SO_2$ scrubber. The particulate scrubbers are 316 L stainless steel and the piping systems are all rubber-lined.

The entire boiler flue gas flow of 927,000 acfm (at normal conditions) is passed through the three scrubbing trains. In the particulate scrubbers the hot flue gas is contacted with river water, removing the majority of the particulate as a 2% aqueous slurry. In this step the gas is adiabatically cooled from 300-330F to 125-130F. Most of the hydrogen chloride, a variable fraction of the sulfur trioxide and a minor amount of the sulfur dioxide contained in the flue gas are absorbed in the scrubbing liquor. This absorption results in a lowering of the liquor pH, which is controlled at about three (3) by the addition of caustic soda in order to prevent corrosion of the 316 L stainless steel. As a further step in preventing corrosion, the liquor blowdown rate is set at a rate so as to maintain the chloride ion concentration below 1000 ppm. The particulate scrubber blowdown is neutralized and sent to the station ash settling basin. The overflow from the ash settling basin goes to the waste water treatment plant and is finally discharged to the Delaware River.

In the $SO_2$ scrubber the flue gas emerging from the particulate scrubber is contacted with a 5-10% aqueous slurry of magnesium sulfite ($MgSO_3$) to remove better than 90% of the sulfur dioxide in the flue gas. In this step the insoluble magnesium sulfite is converted to soluble magnesium bisulfite ($Mg(HSO_3)_2$). In the scrubber surge tank, a slurry of slaked magnesium oxide ($MgO$) is added to the circulating scrubber liquor at a rate sufficient to maintain the pH at about 6.3. The addition of $MgO$ converts the $Mg(HSO_3)_2$ to insoluble $MgSO_3$. A bleed stream from the circulating scrubber slurry goes to a thickener, centrifuge, rotary kiln circuit, where the $MgSO_3$ is recovered as a dry product (Figure 4). The mother liquor recovered from this operation is used to slake the $MgO$ and to wash the scrubber mist eliminators.

The dry $MgSO_3$ is calcined in a fluid bed reactor in the off-site regeneration facility (Figures 5 & 6). This facility includes an air preheater, cyclone separator system, venturi scrubbing, gas cooling tower, drying tower, and mist eliminator for separation of the MgO crystals, and the cleaning, cooling and drying of the $SO_2$ rich gas for transfer to the sulfuric acid plant. This facility was originally located at the OLIN Corporation sulfuric acid plant in Paulsboro, N.J. However, when this plant was permanently closed down in late 1975, the regeneration facility was relocated to the ESSEX CHEMICAL sulfuric acid plant in Newark, New Jersey. The transfer of dry material, MgO and $MgSO_3$, between Eddystone and Newark is by truck transportation.

Standard design parameters for the particulate and $SO_2$ scrubbers are summarized in Table 1.

## OPERATING EXPERIENCE

The availability of the two Environeering particulate scrubbers continues to improve with additional on line experience and is now approaching the 60-75% level. The Peabody-Lurgi particulate scrubber has exhibited a lower availability (approximately 25%), primarily due to excessive vibration of the downstream induced draft fan, due to the accumulation of solids on the rotor. This effect is believed to arise from faulty mist eliminator performance and is discussed at greater length in the next section.

A test program was initiated in June of this year to determine the effectiveness of the scrubbers in removing particulate matter. During the test period the station operated at or close to capacity (310 MW) and burned West Virginia-Pennsylvania bituminous coal of the following average composition.

Average Coal Composition
During Test Program

| Component | |
|---|---|
| Moisture, % | 5.9 |
| Ash, % | 9.4 [a] |
| Sulfur, % | 2.6 [a] |
| HHV, btu/lb | 13,600 [a] |

a - Dry Basis

The results to date indicate that all three scrubbers have the capability of meeting the Pennsylvania particulate emission standard of 0.1 lb/MM Btu at the design conditions shown in Table 1. Chemical analysis of the particulate passing through the scrubbers indicates that soot from the oil-fired reheat burners accounts for about 20-40% of the trapped material. This relatively large contribution is understandable in view of the 100F reheat used at Eddystone in order to avoid a visible plume. (Eddystone Station's location near the end of the main runway of the Philadelphia International Airport gives rise to this requirement.) Sulfate ($SO_4^=$) accounts for another 30-50% of the particulate passing through the scrubbers. Since this large amount of sulfate can only come from scrubbing liquor passing through the mist eliminator, there is a strong presumption that their performance is less than perfect. On occasion the combined effect of this sulfate leakage and the reheat burner soot contribution caused the particulate leaving the scrubber to exceed the 0.1 lb/MM Btu emission standard.

Gas flow rates were varied from 250,000 to 425,000 acfm and the $\Delta P$ from 10 to 18 in $H_2O$ in the particulate scrubbers. Little variation in particulate removal efficiency was noted over this range of conditions. It should be pointed out that the Eddystone scrubbers were retrofitted and that there are very few straight runs of ductwork in the system. As a result, representative sampling of the flue gas, especially for particulate matter, has proved difficult and the reproducibility of the test results has not been of a high order.

The two Environeering scrubbers each have operating times of about 8,000 hours. The Peabody-Lurgi scrubber operating time is about 2400 hours.

The availability of the $SO_2$ scrubber since starting up last May has been about 32%. The longest continuous run to date has been 140 hours. This experience is far from satisfactory but is slowly improving. The several mechanical problems that have contributed to this low availability are discussed in the next section. No fundamental problems involving the scrubber chemistry have been observed.

In spite of the limited availability of the scrubbing unit, a fairly extensive test program to determine the effect of the principal operating variables (L/G, $\Delta P$, pH) on $SO_2$ removal efficiency has been partially completed. At the design conditions listed in Table 1, the $SO_2$ removal efficiency has been shown to exceed 95%. Measurement of the $SO_2$ concentration in the flue gas after a single stage of scrubbing indicates 85-90% $SO_2$ removal efficiency. These results were obtained when the pH of the scrubbing liquor was maintained at 6.3. When the pH was adjusted to 5.8, the $SO_2$ removal efficiency was slightly lower due to the greater equilibrium $SO_2$ partial pressure of the scrubbing solution, but still exceeded 90%. Preliminary results at a pH of 6.8 show performance comparable to that observed at 6.3.

It is not yet possible to make an accurate material balance around the system, so MgO consumption factors are still speculative. Oxidation of sulfite, because of the intermittent nature of the operation has been fairly extensive and recently has been running around 15%. Fairly clear evidence has been obtained that the magnesium sulfite precipitating in the $SO_2$ scrubber surge tank is the hexahydrate ($MgSO_3 \cdot 6H_2O$). As has been shown by Radian Corporation (private communication) the hexahydrate, although less thermodynamically stable than the trihydrate ($MgSO_3 \cdot 3H_2O$) under the prevailing operating conditions, tends to crystallize from solution much more rapidly than the trihydrate. As the blowdown from the surge tank passes through the thickener, a partial conversion of the hexahydrate to the trihydrate is observed. By the time the sulfite is filtered in the centrifuge conversion of the hexahydrate to the trihydrate is virtually complete. No difficulty has been experienced in processing the fine-grained trihydrate through the centrifuge and dryer.

Some 208 tons of dry $MgSO_3$ have been processed through the fluid bed regenerator at ESSEX CHEMICAL, Newark, N.J. so far. The resulting MgO has been returned to the scrubbing process in admixture with make-up MgO. A test run utilizing regenerated MgO only is planned for the near future. Experience to date with regenerated MgO shows that it has a very small particle size, mainly less than 10 microns, and is more reactive than the virgin MgO.

## OPERATING PROBLEMS - PARTICULATE SCRUBBING

### Reheat Burners

The three (3) reheat burners consist of an oil torch mounted in a separate combustion chamber at right angles to the flue gas duct upstream of the scrubber booster fans. The combustion chamber is five (5) foot in diameter, eight (8) feet long and double-brick refractory lined. This refractory has failed due to the criticality of torch placement and start-up problems with the ultra-violet flame scanners. Replacement by a plastic refractory in the 1-B train has shown encouraging performance improvement. An investigation is in progress on the use of a reduced heat load during start-up to limit the thermal shock on refractory.

Burner flame-outs during precipitation have been particularly troublesome. Provision of additional protection for the burner control system has alleviated this situation.

### Mist Eliminators

Mist eliminator performance has not yet been directly measured although plans to do so are now being formulated. However, there is a considerable body of indirect evidence from which the performance can be inferred. The first pertinent observation concerns the operation of the downstream booster fans. All three fans have shown a tendency to accumulate solids on their rotors and to eventually exhibit excessive vibration. The fact that the solids tend to stick to the rotor argues for the presence of moisture in the gas, even after passage through the reheat burner. This situation would be expected if large droplets are passing through or being re-entrained in the mist eliminator. A second observation is the presence of 30-50% sulfate in the particulate trapped from the gas after the reheat burner but in front of the inlet to the booster fans. In as much as the sulfate content of the fly ash entering the scrubber is only 3-8%, it seems reasonable to conclude that the remaining sulfate comes from scrubber liquor (2000-5000 ppm $SO_4^=$) passing through the mist eliminator with the water undergoing evaporation in the reheat burner. The amount of sulfate collected suggests that the liquid loading of the gas after the mist eliminator significantly exceeds 1 gr/scf. A third observation is the high solids deposition rate in the horizontal section of duct following the reheat burner. These solids resemble the particulate trapped from the gas in front of the fan and the amount of it seems consistent with substandard mist eliminator performance. The situation with the Peabody-Lurgi scrubber is particularly severe, to the point where the fan has to be cleaned every few days. Serious consideration is being given, therefore, to replacement of the existing mist eliminator with a more effective product. Consideration is also being given to the installation of pre-demisters in the two Environeering scrubbers. It should be mentioned that the overall problem is aggravated by the relative inefficient mixing of the hot reheater gas with the colder scrubber exit gas. Evidence of this poor mixing is to be found in the pattern of solids deposition in the duct and measurements of gas velocity profiles across the duct.

## OPERATING PROBLEMS - $SO_2$ SCRUBBING

### MgO Slaking

The MgO powder is dispersed in a BIF detention type slaking unit (referred to as the preslaker). Initial efforts to use recycle mother liquor for this purpose resulted in scaling and plugging problems, both in the preslaker and slaker, as well as in the transfer lines and pumps leading to the $SO_2$ surge tank. Therefore, this approach was abandoned for the moment in favor of using fresh water. With this change the dispersion of MgO has been relatively trouble-free but the net result has been an increase of the MgO loss to the waste water blowdown. Therefore, the problem of dispersing MgO in mother liquor has been investigated in the laboratory and hopefully a new procedure has been devised which will permit the direct use of mother liquor in the preslaker. A plant test of this procedure will be instituted in the near future.

Currently the concentrated slurry (20%) of MgO in fresh water is diluted with mother liquor in the slaking tank to a 10-12% slurry, which is fed to the $SO_2$ scrubber surge tank to mantain pH control. Although no deliberate effort is made to slake the MgO since this is not required for the process, the finaldispersion contains slaked MgO in the form of magnesium oxysulfate of somewhat indefinite composition.

### Rotary Screw Feeders

Initially considerable difficulty was encountered with the rotary valves used to transfer solids from the dryer and the cyclone separators to the MgO pneumatic transfer line. The difficulty usually took the form of solids pluggage and/or excessive air leakage. Careful alignment of the feeders and adjustment of clearances has mainly alleviated this problem.

### Circulating Pumps

These pumps are high capacity (6700 gpm) slurry pumps with a water injection packing gland, and the packing develops a sizable leak in a relatively short period. Efforts are being made to reduce this leakage without at the same time causing a large increase of fresh water into the scrubbing system.

### Dryer

In the initial operation period the temperature of the combustion gas entering the rotary kiln dryer was too low because of an improperly sized tip on the oil burner. This resulted in a soot problem which carried through to the $SO_2$ scrubber surge tank and the thickener, since the dryer off-gas is directed to the $SO_2$ scrubber. Evidently incomplete combustion of oil led to the formation of surface active agents, which caused poor settling in the thickener and foaming in the surge tank. Addition of a silicone anti-foaming agent corrected this situation, however, raising the oil combustion temperature caused it to disappear altogether.

## OPERATING PROBLEMS - MgO REGENERATION

Operation of the MgO fluid bed regeneration unit has been hindered by two problems. The first problem is the presence of a Brinks mist eliminator following the drying tower to protect the acid plant from sulfuric acid mist formed in the cooling and drying of the $SO_2$ product gas from the regenerator. Unfortunately a small amount of MgO solid passes through the venturi scrubber provided to protect the downstream operation from particulate contamination. This fine powder quickly plugs the Brinks unit, limiting operation to a day or two. Corrective action taken has been the installation of an irrigated spray-catcher filter after the cooling tower. The effectiveness of this step is now being evaluated. An alternate approach is the use of a wet electrostatic precipitator following the cooling tower and this will be tried later on in the test program.

The second difficulty concerns the air preheater, where the MgO laden gas from the regenerator gives up some energy to the incoming combustion air. When this heat exchanger is allowed to cool below the sulfuric acid dew point of the regenerator off-gas, MgO and/or magnesium sulfate show a tendency to adhere to the tube surfaces. Process conditions have been modified to avoid this situation and hopefully the problem will correct itself.

## PROCESS ECONOMICS

### Capital Cost

The total capital cost for the version of magnesium oxide scrubbing system installed at Eddystone is estimated to be about $130 per kilowatt. This figure includes particulate scrubbing, $SO_2$ scrubbing, MgO regeneration, and facility for converting $SO_2$ to sulfuric acid. Also included is about a $20 per kilowatt retrofit charge associated with the Eddystone installation.

The scrubbing system design is being currently updated to reflect information gained from the present test program. The opportunity to simplify the rather elaborate system initially installed at Eddystone points towards some measure of capital cost savings for future MgO scrubbing installations.

### Operating Cost

The operating and maintenance cost of the Eddystone scrubber system under normal operating conditions is estimated at about 2.3 mils per kilowatt hour, excluding any credit for the by-product sulfuric acid. If credit is taken for the by-product acid, then the O&M cost drops to about 2.0 mils per kilowatt hour. A fairly significant part of the operating cost derives from the 100 F reheat used at Eddystone. Use of a more normal 40 to 50 F reheat would reduce the cost an additional 10%. Other savings, such as reduced power consumption, are anticipated as the system is further optimized.

## PROJECTED SCHEDULE

The shutdown of the OLIN Sulfuric Acid Plant and the need to relocate the MgO regenerator facility to the ESSEX CHEMICAL Sulfuric Acid Plant resulted in an 18 month delay in our test program. The program is now scheduled for completion by mid 1978.

The particulate and sulfur dioxide removal system described here on Eddystone unit 1 is the first phase of a two-phase project. Following the successful line-out of this system with operation at 90% or more availability, it will be incorporated into the design for the complete sulfur dioxide removal on Eddystone Unit 1, and particulate and sulfur dioxide removal on Eddystone unit 2 and one or two units at our Cromby station.

## Table 1

## EDDYSTONE GENERATING STATION UNIT 1
## PARTICULATE AND $SO_2$ SCRUBBER DESIGN PARAMETERS

| Parameter | Particulate Scrubber | $SO_2$ Scrubber |
|---|---|---|
| Gas Flow, acfm - inlet | 321,000 | 268,000 |
| - outlet | 268,000 | 276,000 |
| Circulating liquor, gpm | 1,300 | 13,384 |
| L/G, gpm/1000 acfm outlet | 4.85 | 48.5 |
| pH | 2.8-3.1 | 5.8-6.8 |
| $\Delta P$, in $H_2O$ | 10-12 | 10 Total<br>(5 per stage) |
| Reaction tank residence time |  |  |
| - recirculation, min | 3 | 4.5 |
| - blowdown, hr | 0.55 | 11.0 |
| Particulate, [a] lb/hr - in | 200 | 30 |
| - out | 30 | 30 max |
| $SO_2$ removal, % | - | 90 min |

a - Wet scrubber is preceded by mechanical and electrostatic particulate collectors

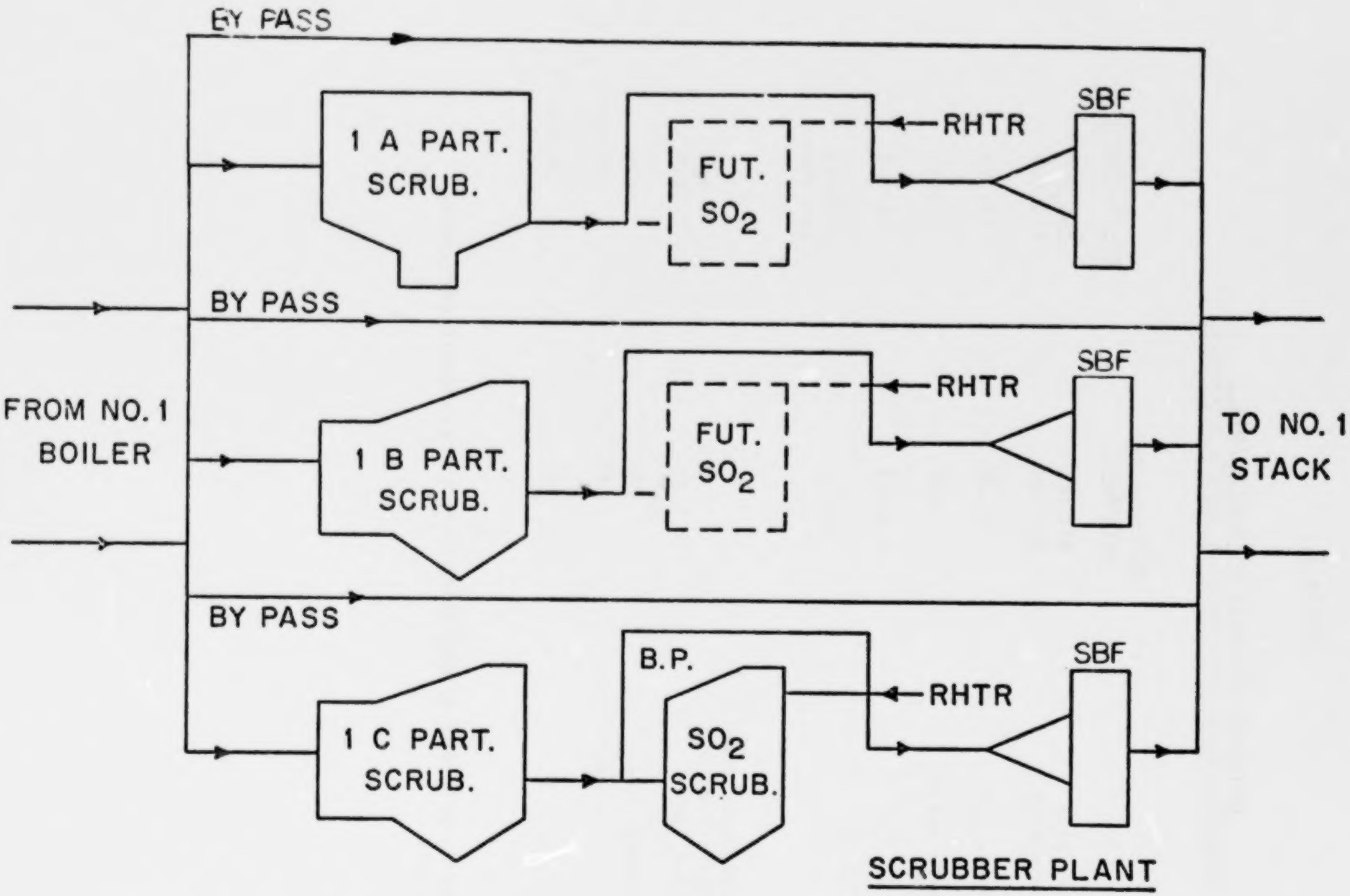

Figure 1. Eddystone no. 1 $SO_2$ removal - phase I.

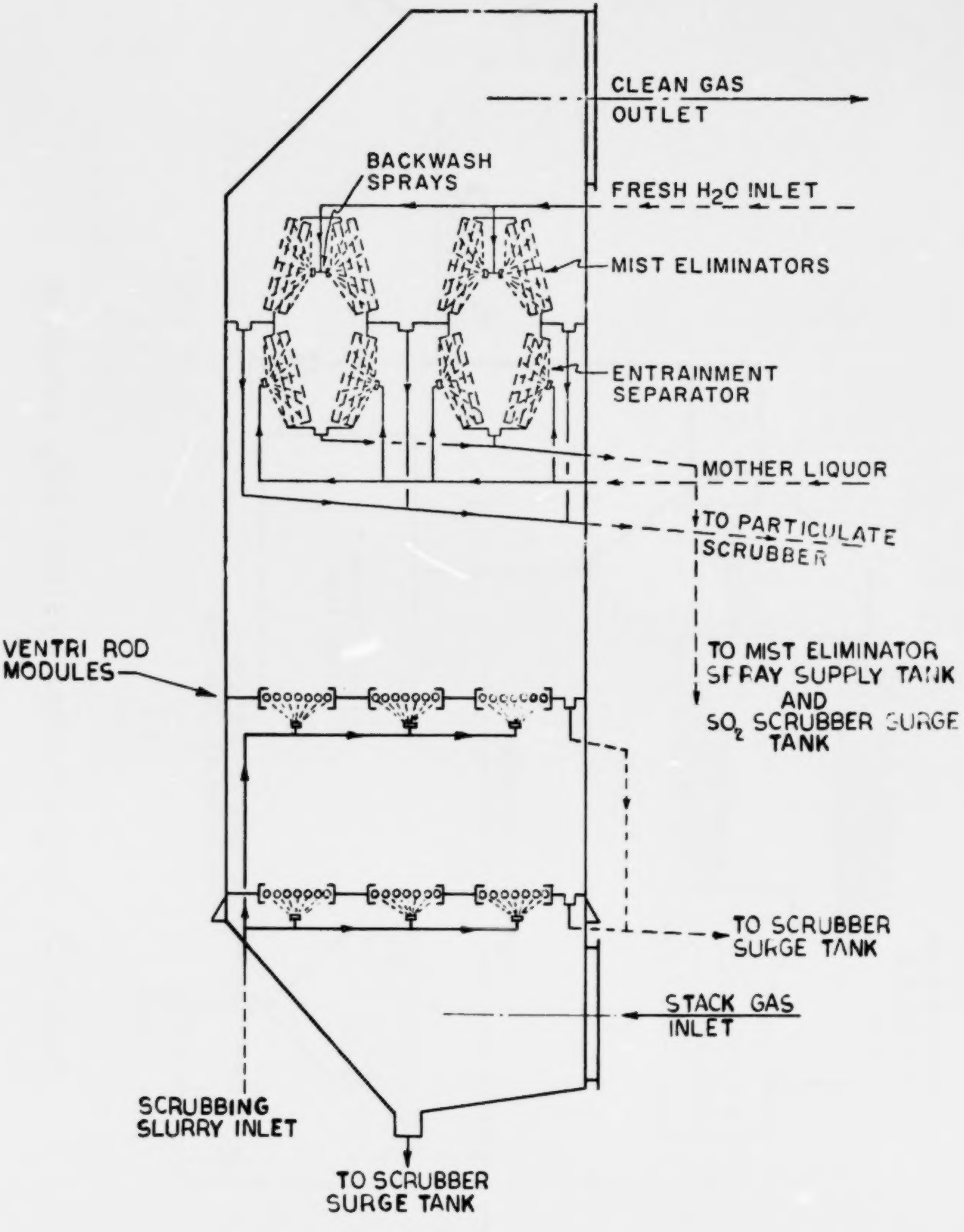

FIGURE 2. $SO_2$ SCRUBBER UNIT DETAIL

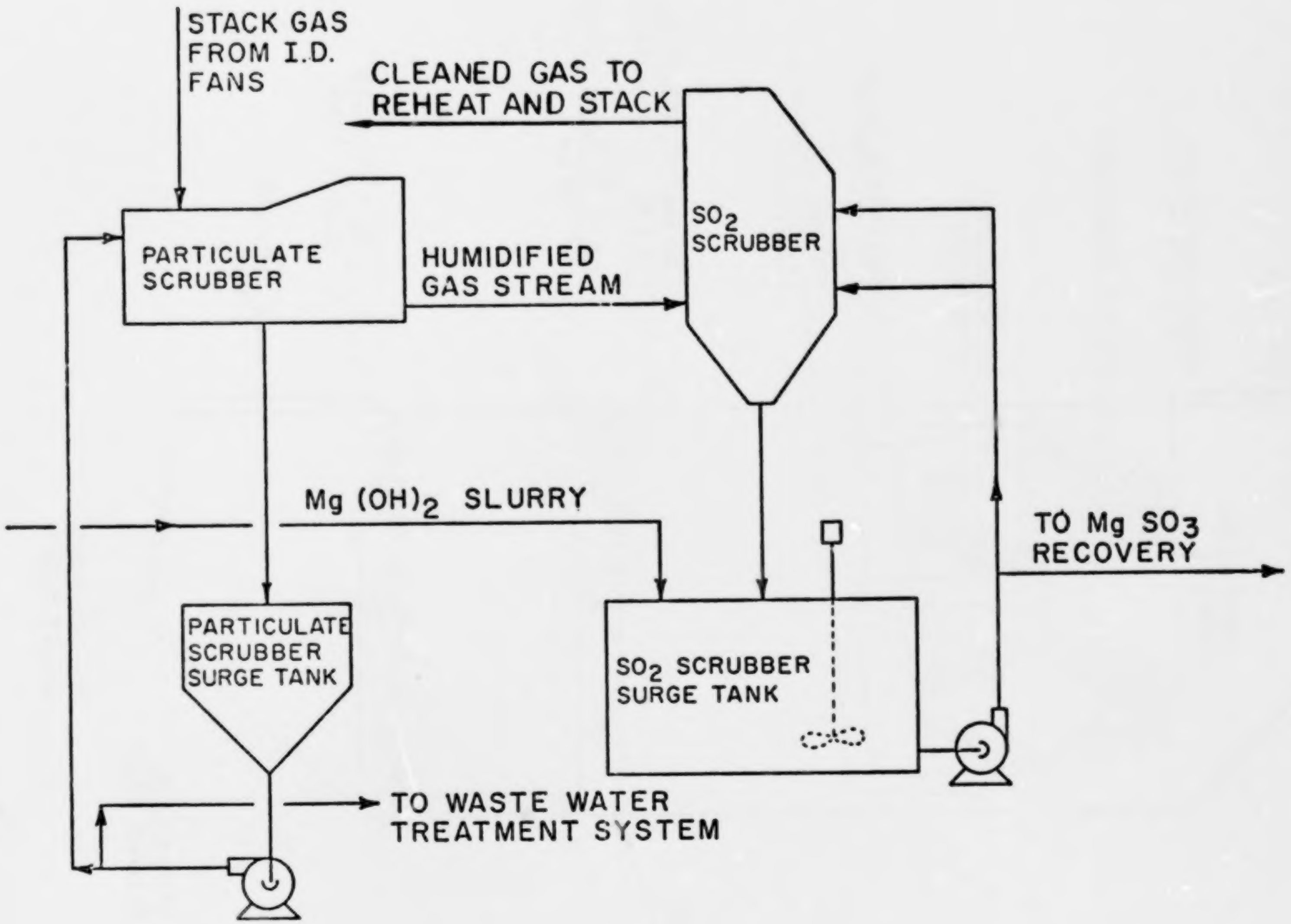
STACK GAS FROM I.D. FANS
CLEANED GAS TO REHEAT AND STACK
PARTICULATE SCRUBBER
HUMIDIFIED GAS STREAM
$SO_2$ SCRUBBER
Mg $(OH)_2$ SLURRY
TO Mg $SO_3$ RECOVERY
PARTICULATE SCRUBBER SURGE TANK
$SO_2$ SCRUBBER SURGE TANK
TO WASTE WATER TREATMENT SYSTEM

Figure 3 $SO_2$ scrubber system - $SO_2$ scrubber.

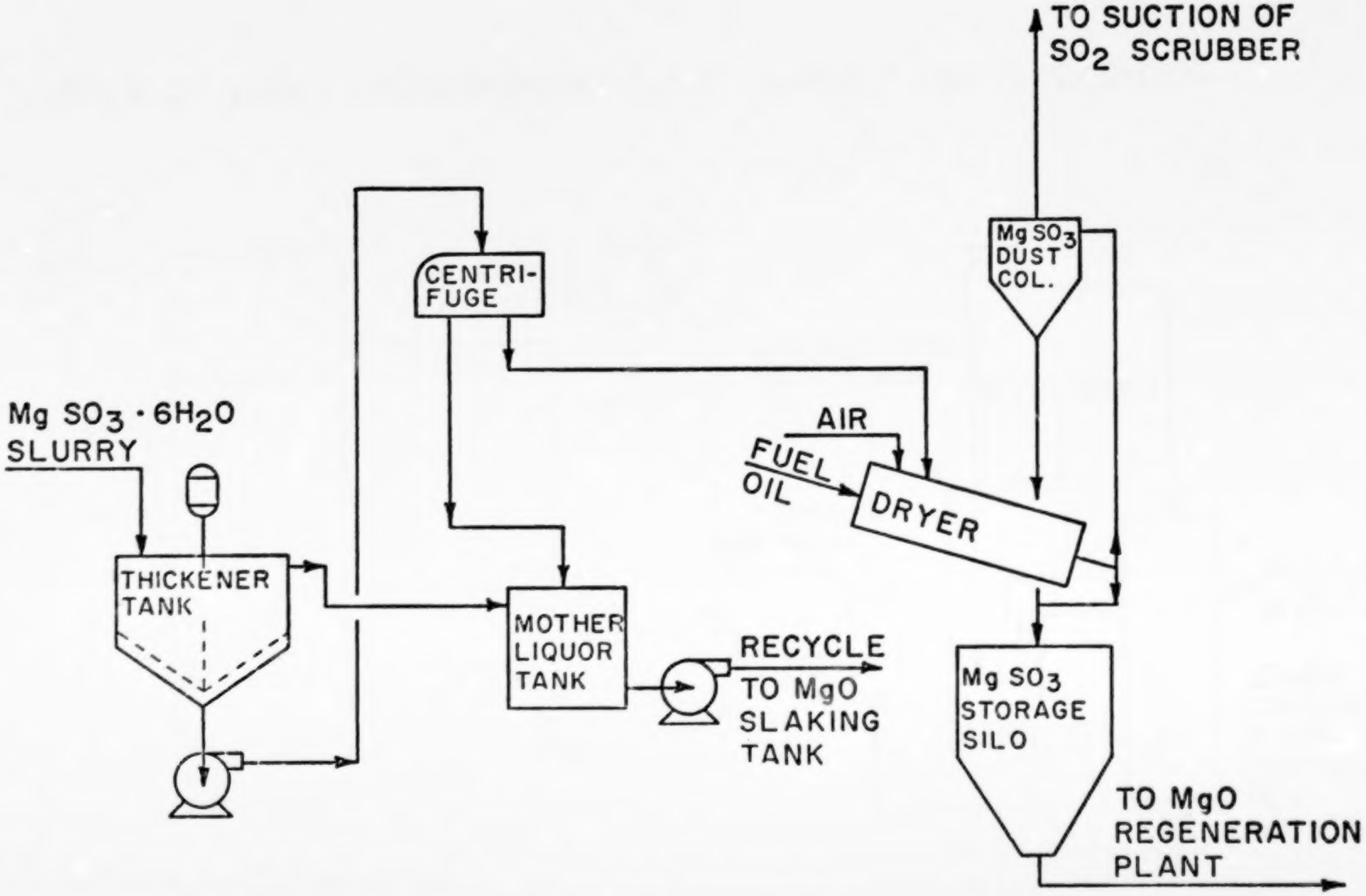

Figure 4 $SO_2$ scrubbing system - $MgSO_3$ recovery.

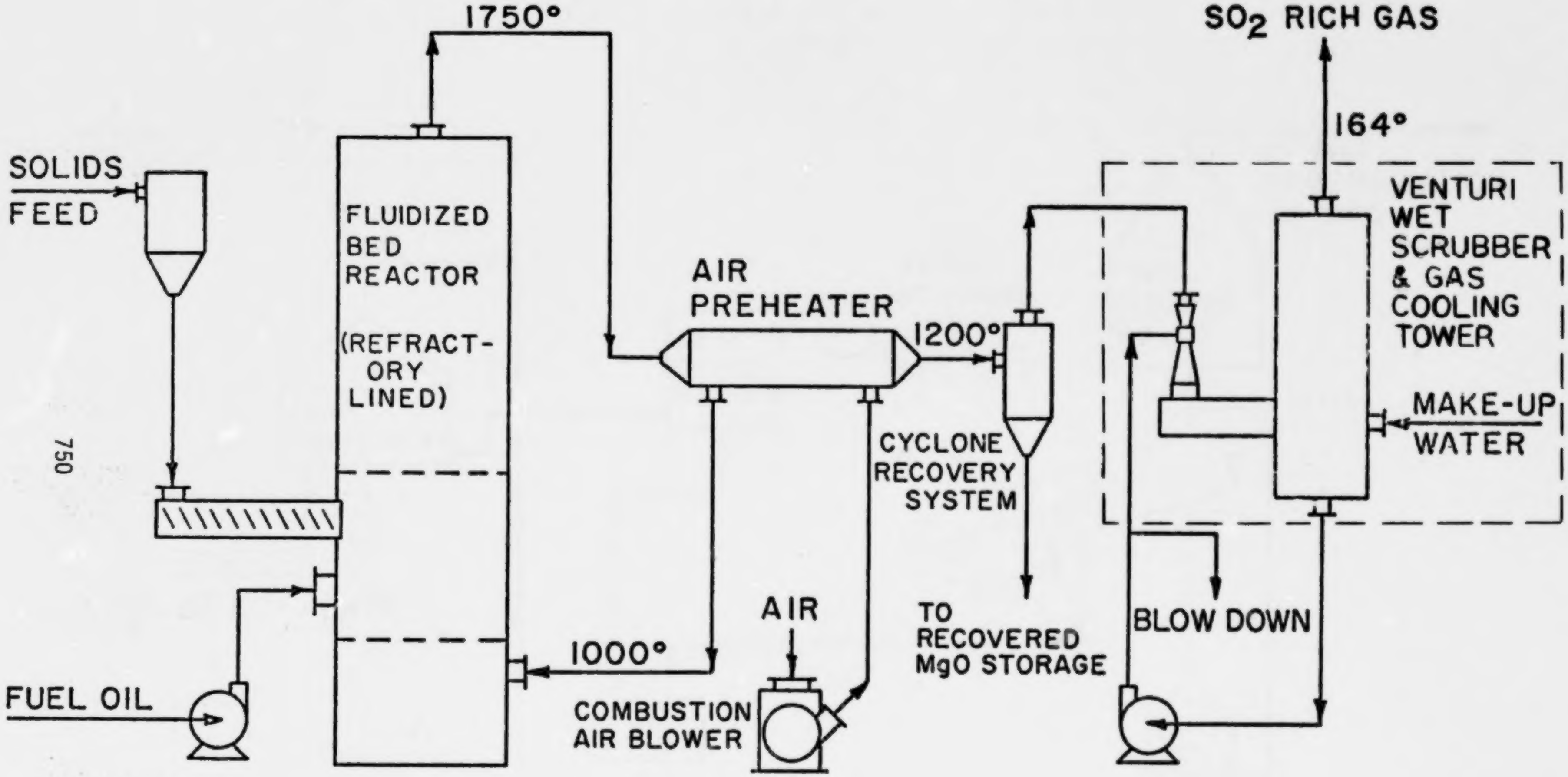

Figure 5. MgO regeneration plant - $MgSO_3$ decomposition

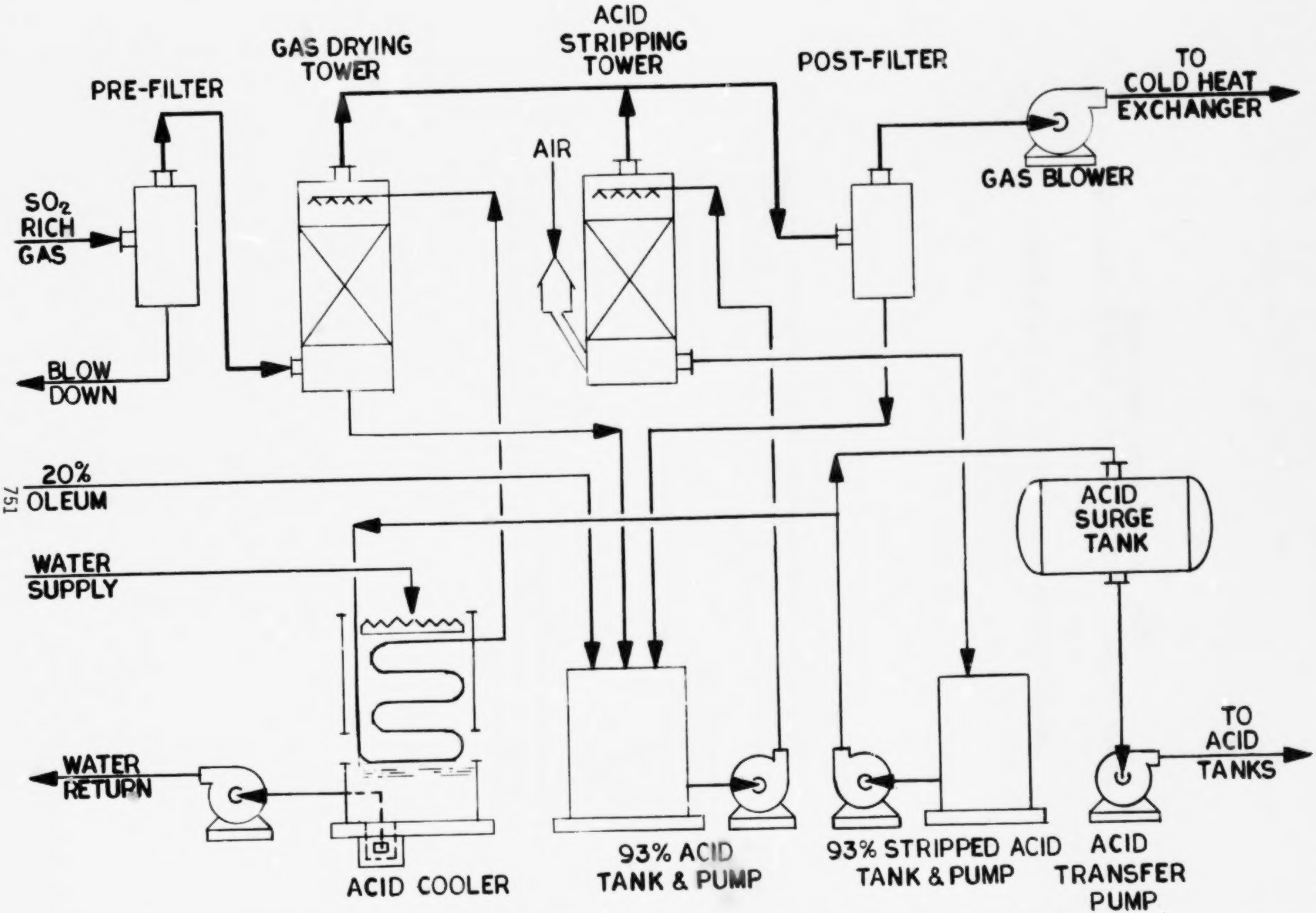

FIGURE 6. MgO REGENERATION PLANT—$SO_2$ CLEANING AND DRYING

# THE SHELL FGD PROCESS PILOT PLANT EXPERIENCE AT TAMPA ELECTRIC

**Allen D. Arneson, Frans M. Nooy, and Jack B. Pohlenz**

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## ABSTRACT

The SFGD process was developed by Shell Internationale Petroleum Maatschappij B.V. (SIPM) (The Hague, Netherlands) for refinery applications to control $SO_x$ emissions from oil-fired process heaters and boilers; the first commercial application is a 40-MW unit in a Japanese refinery. Preliminary experiments with flue gas from coal were carried out at the Galileistraat Station of Rotterdam GEB and gave an indication that the process could be applied to the combustion products of coal as well as fuel oil. A small-scale unit (0.6 MW) was designed, constructed, and placed into operation by UOP in 1974 at Tampa Electric Company's (TECO) Big Bend Station to determine system performance in the presence of coal-derived flyash. This paper details the 2 years of operating experience with this unit. Also included are energy requirements, process economics, and a summary of the developmental status with regard to $SO_x$ reduction, $NO_x$ reduction, and simultaneous $NO_x$-$SO_x$ reduction.

# THE SHELL FGD PROCESS
# PILOT PLANT EXPERIENCE AT TAMPA ELECTRIC

by

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## INTRODUCTION

### Development Considerations

In 1962 Shell Internationale Petroleum Maatschappij (SIPM) initiated a development program to remove $SO_2$ from flue gas containing, besides the usual products of combustion, oxygen and particulate matter. The purpose was to treat flue gas from the combustion of refining residues that are difficult and costly to desulfurize. It was the objective of the development activity that the process utilize a dry, selective adsorbent in order to avoid the complications often characteristic of "wet" systems and require only a modest fraction of the energy transferred in the combustion system being serviced.

It was found that cupric oxide supported on alumina which is stabilized against sulfate formation has outstanding properties for such an application. CuO reacts readily with $SO_2$ and oxygen at 400°C to yield $CuSO_4$ which then can be reduced at the same temperature to yield the sulfur as $SO_2$ (Figure 1), thus permitting a substantially isothermal reduction-oxidation cycle, each step of which is exothermic.

Effective exposure of the acceptor material to the flue gas can be achieved with conventional reactor designs employing moving packed beds, fixed packed beds, or fluid systems. Reactor designs with moving solids have the advantage of providing continuous processing but have the disadvantage of solids attrition, particulate matter separation, and relatively complex solids-handling operations. A fixed, packed bed, however, is not applicable in its usual form since pressure drop would be excessive, and plugging with flyash would be unavoidable. A new fixed-bed reactor design was developed in which the flue gas flows through open channels alongside and in contact with the acceptor material (Figure 2). With this parallel passage design, pressure drop is low, soot and flyash pass through the channels without plugging the bed, and the CuO is effectively presented to the $SO_2$ in such a manner that capture is completed in less than one-half second.

The choice of a fixed-bed reactor results in a cyclic process. When the acceptor becomes loaded with $SO_2$ to the extent that the limiting efficiency is reached, the flue gas flow is directed to another reactor and the reactor containing the spent acceptor is isolated from the flue gas system, purged, and a hydrogen-containing gas is introduced to reduce the copper sulfate. After regeneration the reactor is purged again and is then ready for another acceptance step. Thus, four separate steps can be recognized in the process cycle: oxidation/acceptance, purge, regeneration, and purge.

## Application to Oil-fired Systems

Extensive bench-scale testing defined reaction mechanism, kinetics, and acceptor performance and provided the information required for the design of a pilot plant erected in 1967 in the Shell Refinery at Pernis, near Rotterdam.(1,2) The design of the unit was based on a kinetic model of the parallel-passage reactor internals. The concept of unit cells -- modules containing the acceptor in the parallel-passage configuration -- was developed at this time. The Pernis Plant treated 600-1000 $Nm^3/h$ of flue gas withdrawn from the flue gas duct of a process heater fired with heavy high sulfur residual fuel oil. The stream of concentrated $SO_2$ released on regeneration was not processed further but returned to the flue gas system.

By 1971, over 20,000 hours of operation had been logged on the Pernis unit supported by an associated bench-scale program in the Amsterdam laboratories. Computerized calculation methods had been developed that accurately described process performance; suitable flue gas valves had been selected and their performance demonstrated; construction methods had been developed for the unit cells; and commercial acceptor had been produced and tested.

A 40 MW (equivalent) system was started up in 1973 at the Showa Yokkaichi Sekiyu (SYS) Refinery in Japan. This unit was designed to remove 90% of the $SO_2$ from the flue gas of a refinery boiler fired with heavy high sulfur fuel oil. The Shell Flue Gas Desulfurization (SFGD) section contains two reactors, each capable of processing the entire 125,000 $Nm^3/h$ of flue gas from the boiler and located in parallel with the section of the ducting between the economizer and air preheater. The flue gas is supplied to the reactor section by a fan located in the reactor inlet duct. This configuration provides an open duct across the SFGD section through which flue gas may either by-pass or recycle depending upon the relative rates of flue gas produced and the fan capacity. Thus the turn down of the SFGD is from zero to rated boiler load, and operationally the boiler and the SFGD system are separated. The regeneration off-gas is cooled to condense water vapor and the cyclic flow rate is dampened in an absorber-stripper to yield a concentrated $SO_2$ stream at essentially constant flow rate to an existing Claus unit.(3,4)

## Application to Coal-fired Systems(5,6,7)

Flue gas from heavy oil-fired boilers normally contains 50-300 mg/$Nm^3$ of solid material. Coal-fired boilers, however, produce off-gas with solids contents that may be higher by a factor of 50 to 100. Moreover, the solids compositions differ considerably, and components are present that could affect the performance of the copper acceptor. A two-step program on coal-fired systems was devised to demonstrate (a) the ability of the cell design to operate in a stable manner with high loadings of flyash, and (b) the chemical and physical stability of the acceptor material. As in the demonstration work on oil-fired systems, it was considered necessary to work with flue gas generated in full-scale combustion equipment.

For the first phase a dummy parallel-passage reactor with no provisions for carrying out the acceptance/regeneration cycle was erected next to a coal-fired 57 MW Babcock and Wilcox utility boiler of the "Galileïstraat" Power Station of the Gemeente Energie Bedrijf, Rotterdam, The Netherlands. A slip-stream of flue gas was isokinetically withdrawn from the main duct upstream of the air preheater and the precipitator and passed through a parallel-passage reactor. These preliminary tests yielded encouraging results. The reactor appeared unaffected by flyash loadings up to 20 $g/Nm^3$ and laboratory tests on the acceptor after some 700 hours in flue gas without regeneration showed no loss in activity.

In 1972 a series of meetings took place between representatives of Tampa Electric Company (TECO), Shell and UOP to examine the possibility of TECO participating as a host for an experimental SFGD program. The SFGD process offers several attractive features for application to TECO's operations: water requirements are negligible compared to wet scrubbing; there are no waste disposal problems; and the recovered sulfur could be used by the local phosphate industry. Furthermore, since the experimental unit was to be without shelter, it was advantageous to select a site where the seasonal weather would be favorable. An agreement was completed between TECO and UOP to cover an experimental program at TECO's Big Bend Station located in North Ruskin, Florida. This agreement was consistent with TECO's policy of commitment to assist in the development of FGD process technology and provided UOP with a cooperative host site at a large, modern utility station firing a common bituminous coal (Western Kentucky).

## TECO PILOT PROGRAM

### Design Considerations

To keep the scale small, the design purposely excluded equipment or processing steps that were commercially available and used the simplest reactor design which permits accurate extrapolation of results to full-scale. This decision simplified the plant to the SFGD reactor section only and deleted production of fuel gas for regeneration, flow-smoothing, and work-up (Claus) sections used in a full-scale application.

Considerable effort was made to produce a reactor design that would yield useful information with reasonable expense and time. Critical to this plan was the concept of the unit cell and the single cell stack. In the parallel-passage reactor, flue gas is caused to flow through open channels alongside the acceptor, and contact between the $SO_x$ and the CuO is obtained by radial diffusion of the $SO_x$. This principle has been reduced to practice in modules or cells each of which contains alternating parallel sections of open gas channels and baskets filled with acceptor. Each cell is approximately 0.5 meter square and 1 meter high. Thus, the cross section of each cell determines its flue gas processing capacity (ca. 0.6 MW) and its length determines the capacity for sulfur removal (50 g mol of sulfur). In the usual application a reasonable balance between regeneration frequency and capital cost results in a reactor containing 4 or 5 cells in a single stack and with the appropriate number of stacks in parallel to provide the desired flue gas handling capacity per reactor. In such a reactor, each cell stack operates in exactly the same manner as every other -- adiabatically and independently. Thus, an experimental unit need contain only one cell stack in an adiabatic reactor to exactly reproduce full-scale operation, and by using commercial acceptor and cells the resulting performance information is directly usable in predicting full-scale operation.

The next consideration was directed toward the number of reactors required. The regeneration reaction occurs rapidly and provides a means of synchronizing the cycles of the reactors so that flue gas can be treated at a continuous, constant rate. Before and after regeneration, each reactor is purged with steam. Each reactor is taken from service and returned to service by closing and opening valves located at reactor inlet and outlet. Total elapsed time for valve and purge operation is six minutes per cycle. The minimum time for regeneration is 15 minutes. Thus, a 2-reactor design requires a minimum acceptance time of 21 minutes per reactor, each reactor experiencing the same cycle (Figure 3). Each reactor is in useful service 21/42 or 50% of the time. A design to yield a minimum annual charge may use 3 reactors in acceptance and one in regeneration (Figure 4) and useful service increases to 63/84 or 75% of the time.

Irrespective of the number of reactors employed, each operates with exactly the same cycle and completely independently of others, and in each reactor each cell stack experiences the exact same cycle as all others. Therefore, an experimental unit need contain but one cell stack in only one reactor designed for adiabatic operation.

## Final Pilot Unit Design

A process flow diagram of the TECO pilot unit is shown in Figure 5. Gas can be withdrawn from the flue gas ducts of either Big Bend unit No. 1 or No. 2. Propane burners are installed in long runs of gas ducting to compensate for heat losses. The untreated gas is raised to reactor inlet temperature by heat exchange against treated gas followed by a trim burner on temperature control. The exchanger is a small Ljungstrom with fans located so that leakage is from treated to untreated gas. This exchanger can be by-passed if desired.

The gas rate is controlled approximately by louvers on the suction of the first of two series fans. The gas flow to reactor inlet is provided fine control by throttling the gas which by-passes the reactor with a flapper valve. During acceptor regeneration, the entire gas flow is by-passed. The two fans are fitted in series so that either or both can be operated, depending on the pressure drop over the entire gas circuit, including inlet and outlet ducts. Because the gas rate is small, and with pressure increase related to impeller tip velocity, the resulting rpm of the fans is relatively high (3600 rpm) for this service. During regeneration the reactor is isolated from flue gas by means of flapper valves of the same design as used in the SYS unit. The reactor internals (cells and acceptor) are the same as used in the SYS unit. The operation of the pilot unit was controlled by a solid state electronic sequencer similar to that used at SYS and provides automatic operation.

The unit was constructed in Chicago, mounted on skids, and after pressure testing, moved by truck to Tampa and reassembled on site. Lines were connected and the plant was ready for startup in mid-1974.

The pilot unit was operated for approximately 2 years, during which six runs were made and over 13,000 acceptance and regeneration cycles were performed using the same acceptor loading. A summary of operating conditions for each run is presented in Table 1.

## Experimental Operation

The program initiated at the start of Run 1 was based on the premise that the operation was principally one of demonstration and that few tests would be performed other than to establish acceptor stability with the accumulation of on-stream time. The operating staff assigned to the unit was assembled from the Service Department of the UOP Process Division. In the course of the next few months, after mechanical problems had been resolved, it became clear that the unit was not performing as predicted and that procedures more common to a R&D pilot plant would be required to provide solutions. During this period, for example, specific experiments were required to establish that the seals between cells in the stack were leaking and a portion of the reactor feed was by-passing. The unit was easy to operate, aided by the automatic sequencer, and reliability was good.

At the end of Run 1, operating control of the unit was transferred to the Experimental Development (Pilot Plant) Department of the Division and the program adjusted to provide continuous and detailed monitoring of the operation. The cells were removed and cleaned, the acceptor screened from flyash and reloaded. Samples of the used acceptor were tested in the laboratory for activity. Modifications were made to the seals between cells to prevent gas by-passing and minor mechanical modifications were made to the reactor to simplify procedures for periodically checking seal integrity.

The start-up of Run 2 was made on an air-$SO_2$ mixture with a completely clean system to establish base conditions against which subsequent performance could be compared (Table 1). This turn around procedure and plant calibration was employed at the beginning of each of the rest of the runs. At regular intervals during the entire program (Runs 2 through 6) base operating conditions were re-established (See Table 1) to follow performance as cycles accumulated.

## Process Variable Tests

During the balance of the pilot plant operation process variable tests were made, when convenient to do so, to determine the effects on desulfurization and regeneration performance. It was found that, on the basis of constant acceptance time and constant $SO_x$ concentration, desulfurization efficiency was increased by decreasing the flue gas flow and by increasing the inlet temperature. For a given acceptor loading of sulfur it was found that the instantaneous desulfurization rate is not dependent on inlet $SO_2$ concentration, i.e., the acceptance appears to be first order with respect to $SO_2$ concentration. This information obtained from process variable studies was incorporated into the computer model used to predict acceptance curves showing the relation between the fraction of the inlet $SO_2$ that exits with the treated flue gas and acceptance time. The effects of temperature, channel velocity, and inlet $SO_2$ concentration are shown for the pilot unit in Figures 6, 7 and 8.

## Performance of Parallel-Passage Reactor

In Run 2 (and subsequently in Runs 4 and 5) it was observed that the desulfurization efficiency declined, rapidly at first (down ∿7% in 250 cycles), followed by a slower decay rate and accompanied by a decrease of pressure drop across the reactor (Figures 9 and 10). During the turn around following Run 2, careful inspection of the cells disclosed that the decrease in desulfurization and pressure drop was related to a type of fouling with flyash which tends to smooth the sides of the gas channels. Reduction of surface roughness will decrease the pressure drop, reduce the turbulence in the gas channels, and reduce the radial diffusion rate of $SO_2$.

The experimental program was consequently modified to study this fouling mechansim. In Runs 3, 4 and 5, flyash loading, channel velocity, and flue gas temperature were investigated in that order to determine what effect each might have on this reactor fouling as measured by change in pressure drop. The precipitator on Unit No. 2 is more efficient than that of Unit No. 1 and flyash loadings downstream of this unit are lower than those downstream of the precipitator on Unit No. 1. During

Run 3 no significant decrease of efficiency was experienced. Because of an unscheduled outage of No. 2 boiler, Run 3 was terminated and the SFGD plant was shut down and prepared for Run 4. In Run 4 flue gas was available again from the No. 1 boiler, and the effect of increasing the gas rate was determined. Although initially the rate of efficiency loss was lower, after some 800 cycles efficiencies were again at levels experienced in Run 2.

Run 5 was made with increased flue gas temperatures on the consideration that fouling could be related to acid condensation on flyash particles. When it became apparent that the modest temperature increase possible in the flue gas ducting was having little or no effect, other tests were carried out designed to either arrest the fouling rate or to clean the reactor internals during normal operation. As a part of this program, probes were developed to give an indication of the effect of flyash on reactor performance. These experiments showed that the flyash deposition rate decreased as the flyash loading increased and that a fouled reactor could be cleaned while on stream. This effect was confirmed by operating through several consecutive periods in which the flyash was permitted to accummulate in the reactor as indicated by a decrease in pressure drop and desulfurization followed by on-line cleaning which restored the pressure drop and desulfurization performance to that of start of run. After such a cycle, the run was terminated. Visual inspection confirmed that the internals were clean.

To further demonstrate this solids loading effect, Run 6 was carried out on flue gas taken upstream of the precipitator. While several operating variable studies were made in this Run, there was no decline in efficiency or pressure drop at base conditions over a period of three months and 2200 cycles. It should be noted that during part of Run 6, the flyash loading was well above normal when particulate matter collected in the precipitator was on total recycle to the boiler, resulting in concentrations of 10 grains/SCF (25 g/Nm$^3$), and higher during soot blowing. After completion of Run 6, inspection again revealed that the reactor internals were clean.

TECO Program Summary

After two years of operation, it has been established that:

- The commercial acceptor manufactured by Ketjen* has been demonstrated to be catalytically and physically stable -- 90% desulfurization across a 4-meter bed of acceptor at volumetric space velocities of 5,000/h after 13,000 redox cycles.

- The reactor design has given stable performance with high loadings of flyash; flue gas was processed from the TECO duct upstream of electrostatic precipitators with flyash loadings of 10 grains/SCF (25 g/Nm$^3$). Pressure drop across the reactor and desulfurization performance were unaffected. Techniques were developed to clean fouled internals in situ and during operation.

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*AZKO Chemical, Amsterdam

- The metal oxides in the flyash do not participate in the redox cycle but act as non-interfering inerts. Halogen and/or halogen acids have no effect.
- The mechanical performance of the system was excellent, indicating that the reliability of a full-scale design can be high. Sequence controller, $SO_2$ analyzers, reactor metallurgy, and Adams flapper valves have demonstrated very good performance.

## COMMERCIAL SIZE DESIGN

In the design of a full-scale unit, processing flue gas upstream of the air preheater (Figure 11) will have the advantage that any sensible heat produced in the process is recoverable, and the need for reheat of the flue gas to process temperature is eliminated.(7,8) Since it is not necessary to have flyash removal upstream of the SFGD unit, the flue gas circuit can still use a less expensive cold precipitator. The open, full-line size by-pass around the SFGD unit makes operation of boiler system and desulfurization system completely independent of each other.

### Support Units

For a self-contained SFGD system, such as for a utility application, three additional units are required:

- Flow Smoothing Section
- $SO_2$ Workup Section
- Regeneration Gas Supply Section

Since the process is cyclic, the sulfur dioxide will, during regeneration, be released at an intermittent rate, and it will be diluted with steam. The regeneration off-gas is first cooled and the dilution steam is condensed, raising the $SO_2$ content from 10 vol-% to 80 vol-%. Then the concentrated $SO_2$ is compressed into a gas holding vessel, from which it is released to a workup section on flow control. The workup section may consist of a modified Claus unit to produce elemental sulfur, a fractionation unit to produce liquid $SO_2$, or a sulfuric acid plant. Elemental sulfur is the usual popular choice but not necessarily the economic one.

Regeneration of the spent acceptor can be effected with $H_2$, CO and light hydrocarbons, with the reactivity decreasing in that order. The final form of the reductant is $H_2O$ and $CO_2$. In most cases operating costs can be lowered by taking advantage of the higher reactivity of hydrogen, and consequently CO is shifted and hydrocarbons steam-reformed to hydrogen. Any fuel can be used to produce $H_2$/CO mixtures so the choice of fuel and method is normally one of economics, with the principal costs being those of the fuel used and capital recovery on the equipment.

A study of fuel requirements per unit of $H_2$/CO produced shows that it is the same for steam reforming of straight-run naphtha (desulfurized but unrefined gasoline) and light hydrocarbons ($CH_4$, LPG, light straight run). This value is 450 Btu/SCF of $H_2$/CO which includes both process feed and fuel. Partial oxidation of heavy refining fractions (the fuel oils) has the same thermal requirement as steam reforming. For gasification of fuel oil, coke and coal, the thermal requirement increases to 500-550 Btu/SCF.

Although fuel costs (expressed as $/Btu) are lowest for coal, capital requirements are higher. As applied against the requirements of the SFGD process, the economic choice is steam reforming of hydrocarbons, e.g., natural gas condensate and light straight run naphthas, both of which are used extensively as feedstocks to prepare ethylene, propylene, and synthesis gas due to low octane properties. The availability of such stocks is good. For example, to remove $SO_x$ from flue gas equivalent to 1% S in the coal, the SFGD requirements for naphtha are 1/2 B/D per MW and the amount doubles if the $SO_2$ is converted to elemental sulfur; thus the requirement for 500 MW, 3.5% sulfur coal, 90% desulfurization to sulfur is 1600 B/D. At present more than 300,000 B/D of naphtha is being converted solely to pipeline methane.

## ECONOMICS

Estimated capital and operating costs plus utilities and fuel requirements have been prepared for 90% desulfurization of the flue gas from a 500 MW boiler fired with coal. The sensitivity to sulfur content is shown with three sulfur levels of 3.5, 2.5 and 0.8%. The study basis for all cases is patterned after that used by TVA* and is described in Table 2. Also shown in Table 2 is a tabulation of economic factors assumed for the study. In Table 3 are given the chemical and utility requirements for each case and section by section. Calculation of heat credits and debits to the process is documented in the Appendix.

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*EPA 600/2-75-006

Table 4 presents the estimated capital and annual costs. Capital charge in \$/kW, total operating cost in ¢/kWh, and the total fuel requirements in Btu/kWh, to effect the desulfurization and produce elemental sulfur also are shown in Table 4. It is worthwhile to note that the energy requirements are quite low and compare favorably with non-regenerative (throw-away) processes.

## SUMMARY

The status of the SFGD process development is summarized below:

1. Design, engineering and scale-up procedures have been successfully demonstrated on an oil-fired boiler at SYS of equivalent 40 MW size. With two more reactors identical to the two existing, the equivalent size is tripled to 120 MW with one reactor in regeneration supporting three in acceptance at full load.

2. With the successful demonstration of the commercial acceptor in the parallel passage reactor to process flue gas with high loadings of flyash from a coal-fired boiler, the design, engineering and scale-up procedures employed for SYS are applicable to coal.

3. The special (Adams) flapper valves, cells, metallurgy and control system have given good service.

4. Simultaneous reduction of $SO_x$ and $NO_x$ was begun at SYS in 1975.(9) Reduction of $NO_x$ on coal-derived flue gas has yet to be demonstrated.

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## TABLE 1

# SUMMARY OF BASE OPERATING CONDITIONS ON THE SFGD PILOT PLANT AT TECO

| RUN NO. | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| DURATION, MONTHS | 5 | 2½ | 1½ | 2 | 5 | 3 |
| CYCLES | 2488 | 1520 | 1292 | 1412 | 4328 | 2210 |
| CUMULATIVE CYCLES | 2488 | 4008 | 5300 | 6712 | 11040 | 13250 |
| LOW RATE, SCFM | 1090 | 1090 | 1090 | 1090/1420 | 1090 | 1090 |
| ACC. TIME, MIN. | 20 | 20 | 20 | 20 | 20 | 20 |
| REG. TIME, MIN. | 20 | 20 | 20 | 20 | 20 | 20 |
| FLUE GAS SOURCE* | 1 | 1 | 2 | 1 | 1 | 3 |
| EFF. SOR |  | 92 | 95 | 95 | 95 | 93 |
| EFF. EOR |  | 82 | 95 | 80 | 92 | 93 |

* 1: BOILER NO. 1 DOWNSTREAM OF ESP
2: BOILER NO. 2 DOWNSTREAM OF ESP
3: BOILER NO. 2 UPSTREAM OF ESP

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## TABLE 2
# ECONOMICS OF SFGD SYSTEM
## BASIS

| | |
|---|---|
| ***INCORPORATED UNITS:*** | STEAM-NAPHTHA REFORMER<br>SFGD REACTOR SECTION<br>COMPRESSOR/GASHOLDER FLOW SMOOTH SECTION<br>MODIFIED CLAUS UNIT |
| POWER PLANT SIZE | 500 MW |
| FUEL | COAL |
| S-CONTENT, WT-% | |
| CASE 1 | 3.5 |
| CASE 2 | 2.5 |
| CASE 3 | 0.8 |
| HHV | 10,500 Btu/lb |
| HEAT RATE | 9,000 Btu/kWh |
| EXCESS AIR | 20% |
| AIR PREHEATEAR LEAKAGE | 13% |
| FLUE GAS RATE | 1,582,000 Nm$^3$/h (983,000 SCFM) |
| $SO_2$ CONTENT, ppmv | |
| CASE 1 | 2,580 |
| CASE 2 | 1,850 |
| CASE 3 | 590 |
| MID-1977, GULF COAST LOCATION | |
| LOAD FACTOR | 7,000 h/a |
| CAPITAL CHARGES | 15%/a |
| COST OF: | |
| NAPHTHA | $0.35/gal |
| STEAM (40 psi, SAT.) | $1.50/M lb |
| ELECTRICITY | $0.018/kWh |
| LABOR | $10.00/h |
| HEAT CREDITS | $2.50/MMBtu |
| SULFUR | $45.00/ton |

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## TABLE 3

# ECONOMICS OF SFGD SYSTEM

## ESTIMATED CHEMICALS AND UTILITY REQUIREMENTS

| *CASE 1* | | *SFGD SECTION* | *FLOW SMOOTH SECTION* | *MOD. CLAUS SECTION* | *REFORMER SECTION* | *TOTAL* |
|---|---|---|---|---|---|---|
| ELECTRICITY | ,kW | 5,770 | 850 | 115 | 480 | 7215 |
| STEAM** | ,kmol/h | 1,820 | -380* | -740* | -600* | 100 |
| NAPHTHA*** | ,Gcal/h | | | | 90.92 | 90.92 |
| HEAT CREDITS**** | ,Gcal/h | | | | | 42.53 |
| S° PRODUCED | ,kg/h | | | 5250 | | 5250 |
| *CASE 2* | | | | | | |
| ELECTRICITY | ,kW | 5,800 | 570 | 82 | 330 | 6782 |
| STEAM** | ,kmol/h | 1,300 | -270* | -530* | -415* | 85 |
| NAPHTHA*** | ,Gcal/h | | | | 62.75 | 62.75 |
| HEAT CREDITS**** | ,Gcal/h | | | | | 32.48 |
| S° PRODUCED | ,kg/h | | | 3760 | | 3760 |
| *CASE 3* | | | | | | |
| ELECTRICITY | ,kW | 5,120 | 180 | 30 | 110 | 5440 |
| STEAM** | ,kmol/h | 480 | -95* | -170* | -140* | 75 |
| NAPHTHA*** | ,Gcal/h | | | | 21.01 | 21.01 |
| HEAT CREDITS**** | ,Gcal/h | | | | | 18.46 |
| S° PRODUCED | ,kg/h | | | 1200 | | 1200 |

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* PRODUCED

** 40 psig, SATURATED

*** 5.175 MM Btu/Bbl PRODUCES 11,500 SCF HYDROGEN/Bbl

**** SEE APPENDIX

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## TABLE 4

# ECONOMICS OF SFGD SYSTEM

## ESTIMATED CAPITAL AND OPERATING COST

| *EEC. (MM$)* | *CASE 1* | *CASE 2* | *CASE 3* |
|---|---|---|---|
| SFGD REACTOR SECTION | 28.95 | 28.53 | 22.94 |
| COMPRESSOR/GASHOLDER | 7.82 | 6.10 | 2.65 |
| MODIFIED CLAUS | 2.76 | 2.26 | 1.14 |
| STEAM-NAPHTHA REFORMER | 8.81 | 7.14 | 4.17 |
| *ESTIMATED ANNUAL REVENUE REQUIREMENTS (M$/a)* | | | |
| CAPITAL CHARGES | 7251 | 6604 | 4634 |
| MAINTENANCE | 967 | 881 | 618 |
| LABOR | 123 | 123 | 123 |
| ACCEPTOR | 1479 | 1053 | 411 |
| ELECTRICITY | 909 | 855 | 685 |
| STEAM | 42 | 35 | 31 |
| NAPHTHA | 7174 | 4951 | 1658 |
| HEAT CREDITS | -2977 | -2273 | -1292 |
| SULFUR CREDITS | -1570 | -1126 | -359 |
| *CAPITAL COAST, OPERATING COST, ENERGY REQUIREMENT* | | | |
| CAPITAL COST, $/kW | 97 | 88 | 62 |
| OPERATING COST, ¢/kWh | 0.38 | 0.32 | 0.19 |
| ENERGY REQUIREMENT, Btu/kWh * | 525 | 371 | 124 |

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* DEFINED AS THE SUM OF:

| | |
|---|---|
| ELECTRICITY AT | 9000 Btu/kWh |
| STEAM AT | 40000 Btu/kmol |
| NAPHTHA AT | 4 Btu/kcal |
| HEAT CREDITS AT | 4 Btu/kcal |

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FIGURE 1

BASIC CHEMISTRY OF THE SFGD PROCESS

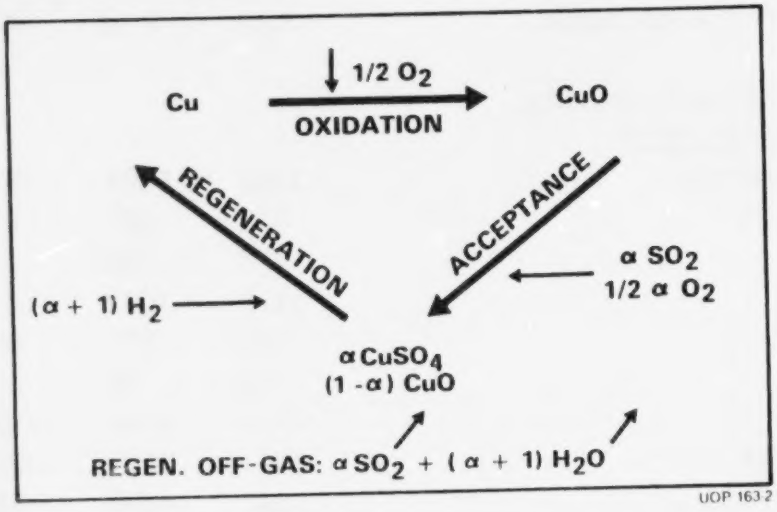
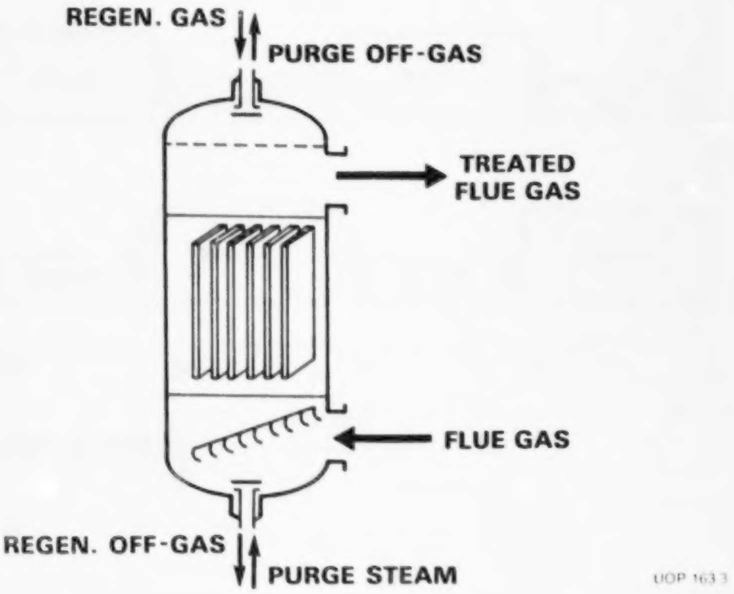


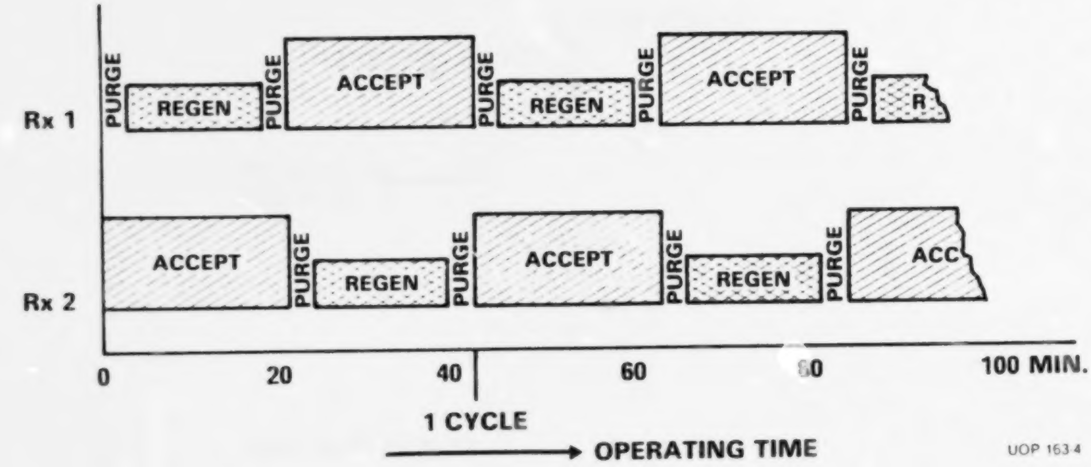
FIGURE 2

THE PARALLEL PASSAGE REACTOR



## FIGURE 3

# TYPICAL OPERATING MODE SEQUENCE IN A TWO-REACTOR SFGD SYSTEM



### FIGURE 4

## TYPICAL OPERATING MODE SEQUENCE IN A FOUR-REACTOR SFGD SYSTEM

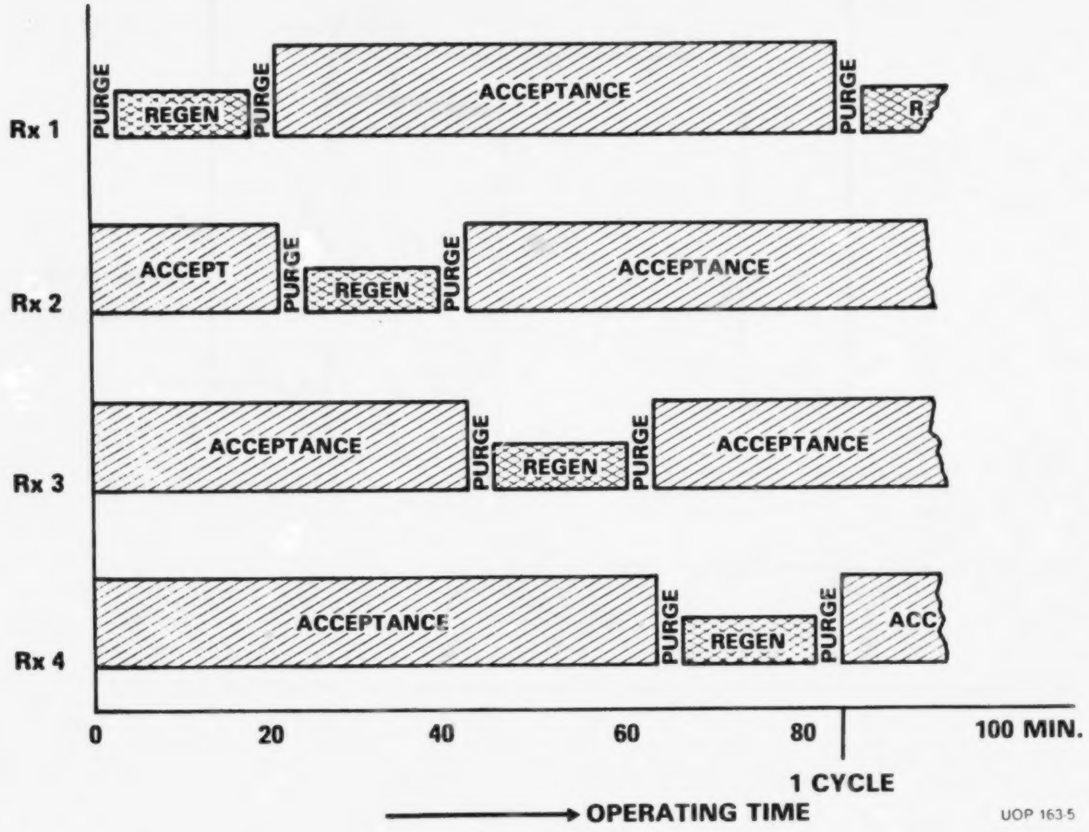


FIGURE 5

FLOW DIAGRAM OF SFGD PILOT PLANT AT TECO

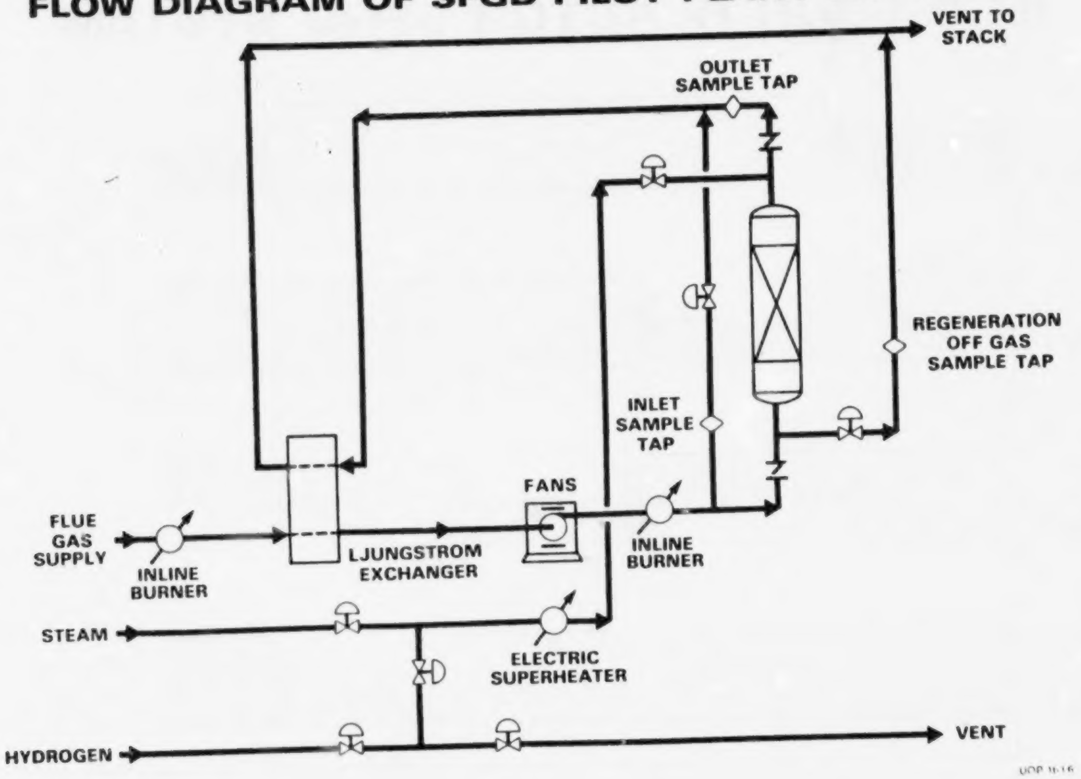
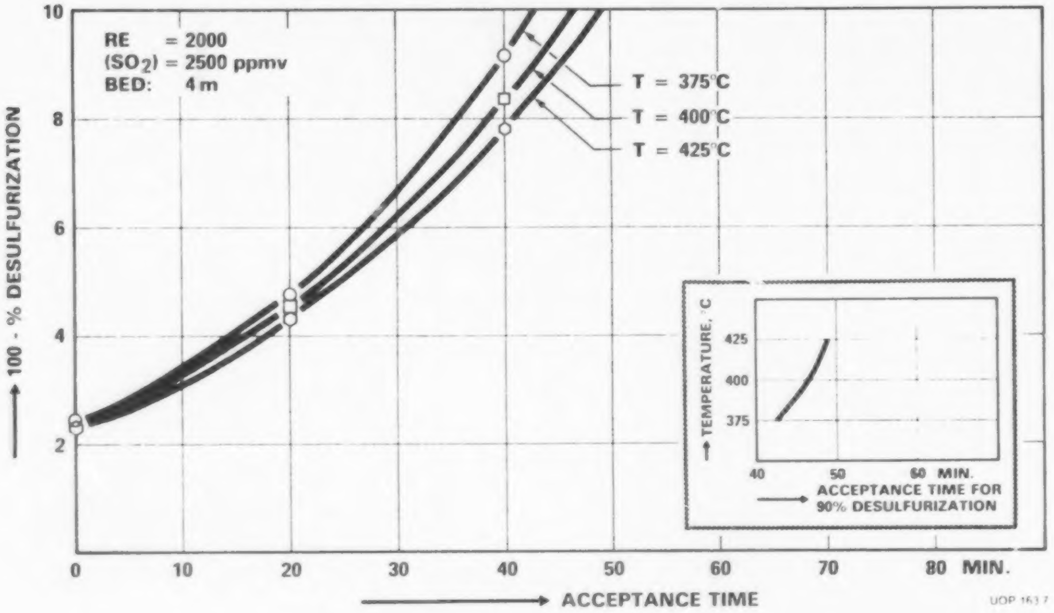


FIGURE 6

## INFLUENCE OF INLET TEMPERATURE ON DESULFURIZATION EFFICIENCY



## FIGURE 7

# INFLUENCE OF INLET $SO_2$ – CONCENTRATION ON DESULFURIZATION EFFICIENCY

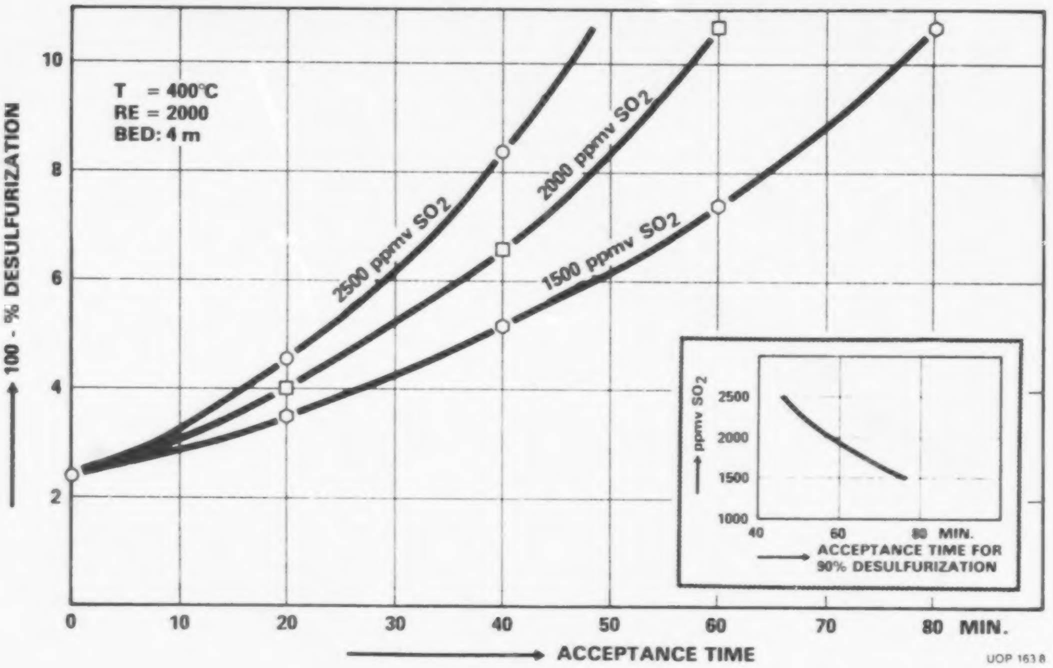


FIGURE 8

## INFLUENCE OF SPACE VELOCITY (RE NO.) ON DESULFURIZATION EFFICIENCY

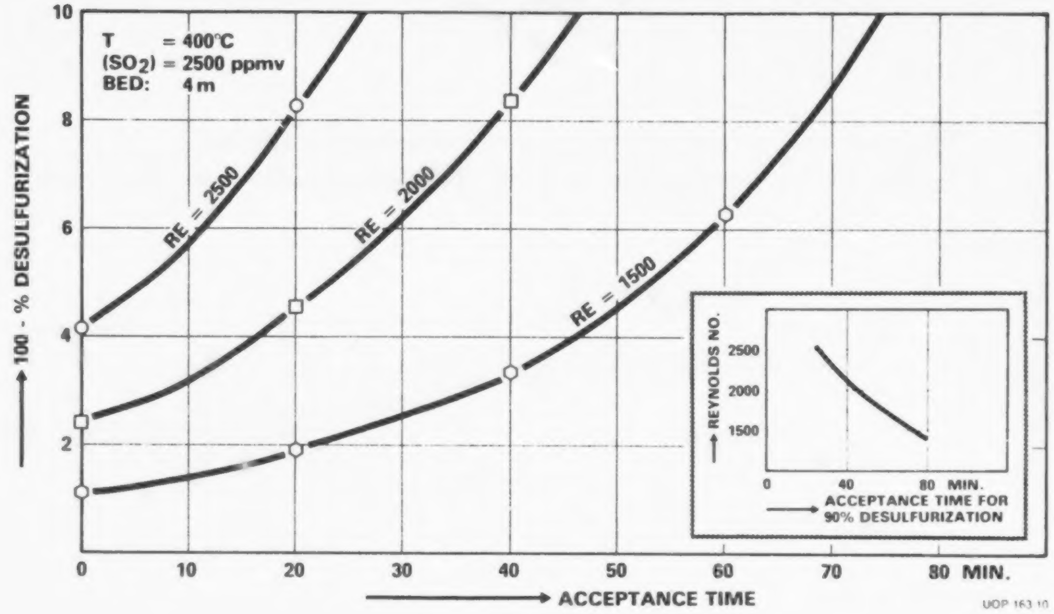


FIGURE 9

$SO_2$ REMOVAL EFFICIENCY vs. CYCLES FROM SOR

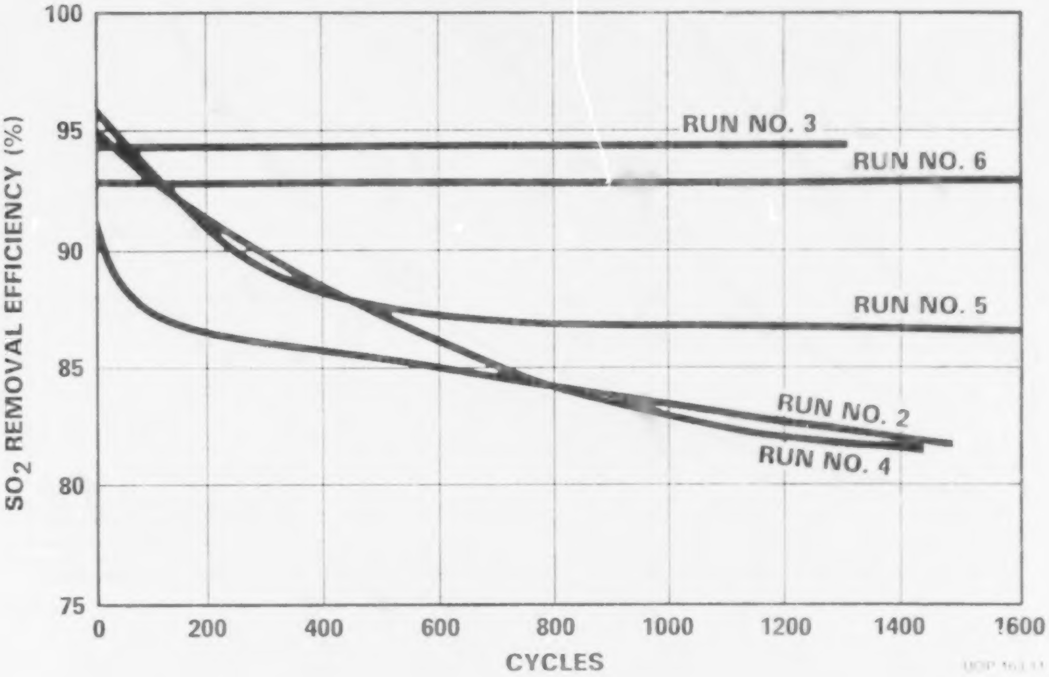


FIGURE 10

$SO_2$ REMOVAL EFFICIENCY AND PRESSURE DROP ACROSS REACTOR IN RUN 4 vs. CYCLES FROM SOR

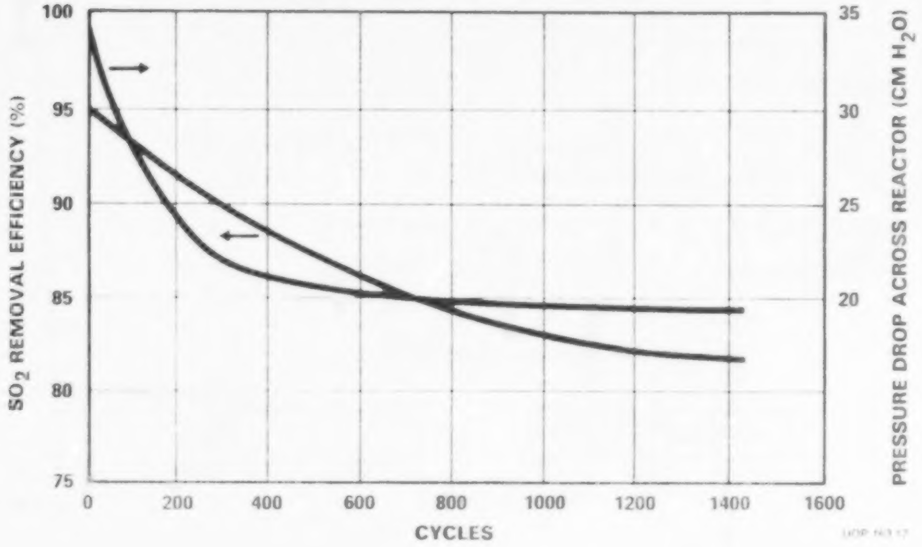
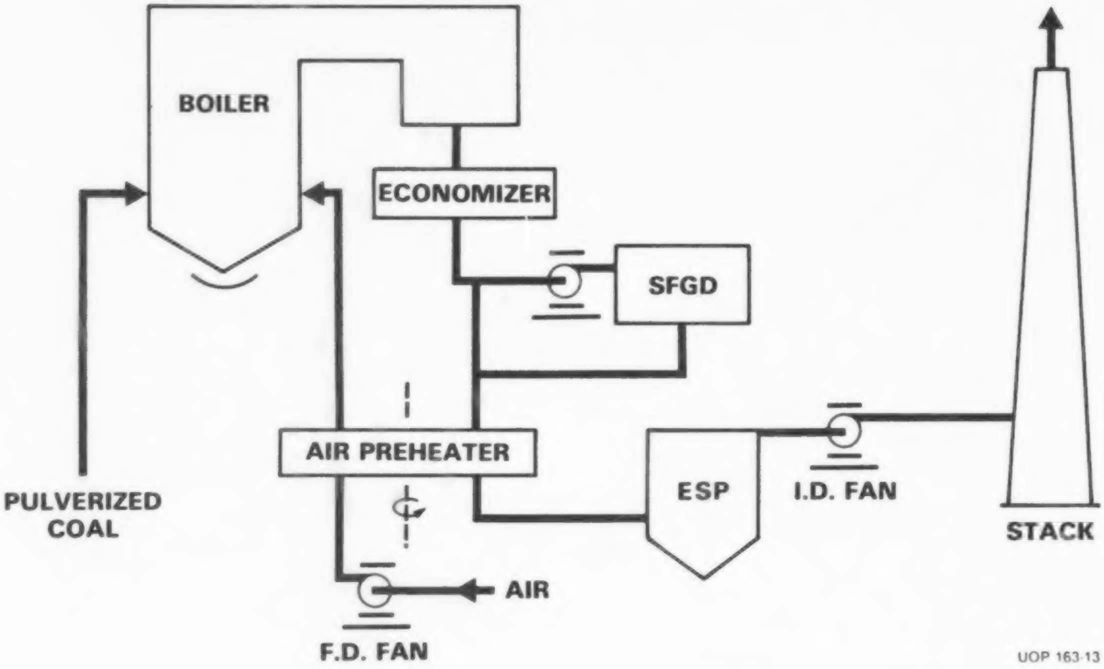


FIGURE 11

## SCHEMATIC FLUE GAS FLOW DIAGRAM OF BOILER SYSTEM WITH FLUE GAS TREATING (SFGD, ESP)



# APPENDIX

## HEAT CREDITS AND DEBITS

When the SFGD system is properly incorporated in the total boiler/furnace design, and is so positioned that process flue gas is drawn from and returned to the flue gas ducting between the economizer and the air preheater, sensible heat produced in the SFGD process is recoverable. Any heat released to the flue gas and purge gas can be recovered in the air preheater, and heat released to the regeneration gas is recovered partly in the waste heat boiler of the flow smooth section. In the table below a listing of the credits and debits is given for the SFGD system for Case 1. These credits and debits are described and calculated in the subsequent pages.

### CREDITS

| | | Gcal/h |
|---|---|---|
| Dewpoint suppression | | 10.64 |
| Fan compression | | 3.72 |
| Reaction heat: | $Cu \longrightarrow CuO$ | 6.88 |
| | $CuO \longrightarrow CuSO_4$ | 12.23 |
| | $CuSO_4 \longrightarrow Cu$ | 0.91 |
| | $CuO \longrightarrow Cu$ | 0.42 |
| Purged gas combustion | | 0.81 |
| Vented gas combustion | | 10.92 |
| Slipped gas combustion | | 0.00* |

DEBITS

| | |
|---|---|
| Steam superheat | -4.00 |
| Total | 42.53 |

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* For the example case the slipped gas combustion credit is not calculated separately. See item in Section 6. The slipped gas credit is incorporated as a reduced fuel gas requirement for the modified Claus workup unit.

* * *

## 1. Dewpoint Suppression

In the process not only the $SO_2$ concentration decreases but also the $SO_3$ content of the flue gas. The dewpoint of the flue gas is determined by this $SO_3$ concentration, and is therefore decreased by the SFGD process. Good energy management prescribes that the flue gas be rejected at temperatures close to the dewpoint. After desulfurization in the SFGD process the flue gas temperature at the air-preheater exit can be lower, and the process can be credited for the extra heat taken from the flue gas.

In Case 1 the flue gas flow is 1,582,000 $Nm^3/h$, with a specific heat of 0.327 $kcal/Nm^3/^{o}C$. The $SO_3$ concentration drops from 77 ppmv before desulfurization to 8 ppmv after desulfurization, and the dewpoint decreases, therefore, from $152^{o}C$ to $131.5^{o}C$. The credit to the process is, therefore, 10.64 Gcal/h.

## 2. Fan Compression

The adiabatic heat of compression, resulting from work done by the process flue gas blower on the flue gas, will result in a flue gas temperature increase. This sensible heat is, therefore, recoverable in the air preheater.

The blower efficiency is about 75%, and the power to the blower motor needs to be 5,770 kW. With a conversion factor of 860.5 kcal/kWh the credit to the process will be 3.72 Gcal/h.

## 3. Reaction Heat

The heats of reaction released during acceptance will result in flue gas temperature increases, and this heat is, therefore, recoverable in the air preheater. The heat of regeneration reaction will be released to the regeneration gas, resulting in a temperature increase of the regeneration off-gas. It is normal to design such that the regeneration off-gas leaves the reactors at 400°C, and this means that less heat is required to superheat the dilution steam to regeneration gas inlet temperature. This heat of regeneration reaction should, therefore, be subtracted from the superheat requirements, but for ease of calculations it is listed as a separate item in the following description of each reaction.

### 3.1. Oxidation (at beginning of acceptance)

$$Cu + 1/2\ O_2 \xrightarrow{400^{o}C} CuO + 37{,}340 \text{ kcal/kmol Cu}$$

The amount of sulfur dioxide removed from the flue gas is 164.0 kmol/h, and the loading at end of acceptance is 0.89. The total copper reacting in the oxidation reaction is (164.0/0.89=) 184.3 kmol/h. The heat released by this reaction, and the credit to the process is 6.88 Gcal/h.

### 3.2. Sulfation (acceptance)

$$CuO + 1/2\ O_2 + SO_2 \xrightarrow{400^{o}C} CuSO_4 + 74{,}600 \text{ kcal/kmol CuO}$$

The amount of sulfur dioxide removed from the flue gas, and the amount of CuO reacting with it is 164.0 kmol/h. The credit to the process is, therefore, 12.23 Gcal/h.

### 3.3. Reduction (regeneration)

$$CuSO_4 + 2H_2 \xrightarrow{400^{o}C} Cu + SO_2 + 2H_2O + 5{,}560 \text{ kcal/kmol } CuSO_4$$

The amount of copper sulfate reacting equals the amount of sulfur dioxide removed, and is 164.0 kmol/h. The credit to the process is 0.91 Gcal/h.

### 3.4. Reduction of Copper Oxide (regeneration)

$$CuO + H_2 \xrightarrow{400^{o}C} Cu + H_2O + 20,880 \text{ kcal/kmol } CuO$$

The amount of copper oxide reduced during regeneration is the difference between the copper oxidized (184.3 kmol/h) and sulfated (164 kmol/h), and equals 20.3 kmol/h. The credit to the process is 0.42 Gcal/h.

### 4. Purged Gas Combustion

At the end of regeneration, when the regeneration gas flow is stopped, and purging of the reactor is started, the reactor is still filled with regeneration gas. This is purged into the flue gas going to the other reactors, and any combustibles present in this gas will be catalytically oxidized, releasing the heat of combustion to the flue gas. The result is an increased flue gas temperature, and the heat is thus recoverable in the air preheater.

In the example Case 1 the credit to the process is 0.81 Gcal/h.

### 5. Vented Gas Combustion

The cyclic process uses reducing (regeneration) gas intermittently. If the design of the system is based on a continuous supply of reducing gas, this gas is diverted to burners during reactor purging (vented).

The process is debited for the continuous charge of reducing gas and credited for the heat of combustion of the vented portion.

For the gas produced in this system the heat of combustion is 68,015 kcal/kmol. The gas vented to burners is 160.5 kmol/h and the credit to the process is 10.92 Gcal/h.

### 6. Slipped Gas Combustion

Since hydrogen is much more reactive in the regeneration (reduction of $CuSO_4$) than CO and light hydrocarbons, it is assumed that only hydrogen participates in the reaction and all other species "slip" or pass through the bed unreacted, and end up in the off-gas from the flow smoothing section. Furthermore, some hydrogen will slip through at the end of regeneration, when the reduction is completed. In downstream $SO_2$ conversion units these combustibles can be used as reductant (modified Claus), or for heating and subsequent steam production. Always the heat of combustion can be recovered, and should, therefore, be credited to the process.

### 7. Steam Superheat

The steam used for regeneration and purging is usually the most inexpensive steam available. The pressure requirement for the steam is only about 40 psig, but the temperature needs to be about 400°C. By means of an indirect heat exchanger the steam superheat is extracted from the flue gas and is debited against the process. (Most of this superheat is recovered from the regeneration off-gas in the waste heat boiler of the flow smooth section. There it appears as a steam credit).

In the example case 1,820 kmol/h steam, 40 psig and saturated, has to be heated to 400°C. The enthalpy increase is 120 kcal/kg and the debit to the process is 4.00 Gcal/h.

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# AMMONIA SCRUBBING PILOT ACTIVITY AT CALVERT CITY

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## ABSTRACT

A 4,000-CFM wet ammonia scrubber was operated at Air Products and Chemicals' Calvert City, Kentucky manufacturing plant. The four-stage desulfurization unit was fed a flue gas slipstream from a 20-MW boiler firing approximately 2.3 percent sulfur coal. Byproduct of the open-loop system (ammonia-sulfur brine) was used as fertilizer. Emphasis throughout the program was placed on engineering optimization.

Catalytic's efforts to identify and resolve problems, particularly those involving particulate emissions in the scrubbed gas, are summarized. Overall system performance, in terms of process chemistry, equipment operation, instrumentation and control, is discussed. An assessment of current status, including projected economics for a 500-MW commercial installation, is also included.

## AMMONIA SCRUBBING PILOT ACTIVITY AT CALVERT CITY

### INTRODUCTION

During the first half of 1976, Catalytic operated a 4,000 CFM ammonia scrubber at the Calvert City, Kentucky chemicals plant of Air Products and Chemicals, Inc., its parent company. This pilot-scale desulfurization system was conceived as an Engineering Optimization Unit; self-contained and transportable. Its chief function was to generate reliable design data by scrubbing representative flue gases containing sulfur dioxide.

A 20-megawatt, coal-fired boiler at Calvert City was chosen as the gas source for initial optimization studies. A six-month program was devised to identify and to solve problems associated with ammoniacal scrubbing in the fumeless mode. Specific objectives of this program were:

- To apply the Air Products/Catalytic fumeless ammonia technology to an actual flue gas derived from coal combustion.
- To assess system viability in critical areas:
  - adaptability to boiler fluctuations
  - mechanical performance and reliability
  - materials of construction
  - maintenance requirements
  - instrumentation reliability
- To establish a viable process control philosophy

The host boiler presented a particular challenge: it was not equipped with an electrostatic precipitator and the flue gas contained more particulate matter than would normally be present in a conventional utility operation. While this incumbent dust impeded Catalytic's attempts to conduct experiments related to ammonia fume formation, it nonetheless helped to demonstrate process flexibility in the presence of coal-derived fly-ash. It also provided valuable operating experience which would not have been gained had a precipitator been installed.

The skid-mounted pilot system contains the basic elements of the commercial scrubber module we visualize: a forced-draft blower, a low-energy venturi humidifier, and a multistage ammoniacal absorption chamber. (It is understood that a commercial scrubbing system of this type would operate in series with an efficient electrostatic precipitator.) The pilot system did not include ammonia regeneration. Spent ammoniacal scrubbing brine (an aqueous solution of ammonium sulfite, bisulfite and sulfate) was removed from the Calvert City site by an agricultural chemicals dealer. The brine was consumed locally as a direct-application fertilizer.

Prior to the Calvert City program, Catalytic and Air Products had performed extensive bench-scale testing of our ammonia technology. Experience in the field, however, had been limited to a brief series of runs at TVA's Colbert Station pilot plant and consultation with operators of ammonia scrubbers. Our greatest concern was to gain practical experience; therefore, our optimization program stressed applications rather than fundamental studies.

This paper summarizes what was learned at Calvert City, largely in terms of the major problems encountered and solved. Instead of a dissertation on ammonia scrubbing, we are attempting to provide a status summary of our ammonia process, and hopefully, a useful guide to those involved in the vagaries of FGD pilot plant design and operation.

## BACKGROUND

$SO_2$ absorption in aqueous ammoniacal solutions is neither new nor complex. The concept was patented as early as 1883(1) and fundamental vapor-liquid equilibrium data for the $SO_2$/ammonia/water system were documented before 1938.(2-6) At least one scrubber has been in service (7) for more than forty years; and numerous others are currently in operation, principally at sulfuric acid plants and sulfite-based pulp mills. In each existing application, ammonia scrubbing was chosen because of its inherent reliability and the utility of its by-products.

About five years ago, Air Products postulated an explanation for the characteristic appearance of aerosols ("blue plumes") in flue gases contacted by ammonia. Laboratory studies (8) confirmed the theory and led to the establishment of "fumeless" design criteria which were subsequently patented.(9)

During April and May of 1973, Catalytic and Air Products participated with TVA and EPA in a factorial series of experiments at TVA's Colbert Station pilot plant. During a run conducted in the fumeless mode, two plume readers certified by EPA concurred that zero opacity had been achieved and maintained. TVA later reported(10) that "plume formation while producing a (spent scrubbing) liquor with high salt concentration...can be controlled by proper operation of the scrubber."

In 1974, experimental flexibility in Air Products' laboratory was greatly expanded by the installation of a four-stage glassware apparatus which contained a Lear-Siegler RM4 Transmissometer. The optical path-length of the Transmissometer (roughly twice the length of a single stage) was 65 inches; consequently it was possible to sense even optically invisible aerosols with precision. Exhaustive testing with simulated flue gases culminated in the ability to make fumes appear (and subsequently vanish) at will, depending only upon whether or not the scrubber was operating within a rigorously defined parametric envelope.

Success on the bench scale led to the next logical step: field testing of the process using actual flue gases and equipment representative of the projected commercial case. Therefore, in 1975, a 4,000 CFM, skid-mounted scrubbing system was installed at Calvert City with the prospect of obtaining necessary optimization and scale-up data. In mid-1976, after six months of operation, this optimization program was concluded. High fly-ash carryover due to non-isokinetic sidestream withdrawal from the host boiler made it impossible to identify quantitatively the sources of particulate emissions from the stack, although it was clearly apparent that the characteristic (persistent and dense) ammonia fume could be "turned off" (or, at least greatly reduced) by scrubbing in the fumeless mode. The less-than-ideal operating conditions did, however, verify the operability and controllability of an ammonia scrubber in a coal-fired application.

Two processes complementary to ammonia desulfurization have been licensed by Catalytic: Institut Francais du Petrole's liquid Claus sulfur recovery system(11) and Chisso Engineering Company, Ltd.'s $NO_x$ removal technology. The IFP process has been successfully tested on a prototype (30 MW) scale in France, while the CEC process has been piloted in Japan with comparable success.(12) Fully integrated, the three compatible process segments comprise a regenerable, closed-loop system, potentially applicable in virtually any flue gas cleanup situation where elemental sulfur is the desired by-product. The combined systems can also be operated to produce a mixed slate of by-products; namely, ammonium sulfate and elemental sulfur. Operated alone, the ammonia scrubber is an economical approach in cases where fertilizer or ammonium sulfate production is acceptable.

## THEORY

The following principal chemical reaction occurs when $SO_2$ is absorbed in ammoniacal brine:

$$SO_2 + (NH_4)_2SO_3 + H_2O = 2\ NH_4HSO_3 \qquad (1)$$

Fresh (or regenerated) ammonia (usually fed to the absorber in aqueous solution) generates the ammonium sulfite:

$$NH_4OH + NH_4HSO_3 = (NH_4)_2SO_3 + H_2O \qquad (2)$$

A small quantity of ammonium sulfate is also produced by reaction with oxidizing agents usually present in flue gas.

$$SO_3 + (NH_4)_2SO_3 = (NH_4)_2SO_4 + SO_2 \qquad (3)$$

$$O_2 + 2\ (NH_4)_2SO_3 = 2(NH_4)_2SO_4 \qquad (4)$$

Noting the frequent but not inevitable generation of "blue plumes" when $SO_2$ is absorbed by aqueous ammonia, studies(8,9) were conducted to determine the source of the offensive particulate and the conditions under which it forms. Two significant findings were confirmed in the laboratory:

(1) Precipitation of ammonia salts in the vapor phase is a function of composition and temperature. Specifically, if the mathematical product of the partial pressures of water vapor, $SO_2$ and ammonia above solutions of scrubbing liquor is maintained below a critical value (which varies inversely with temperature), no particulates appear in the vapor phase. This condition can be expressed as follows:

$$\log_{10} \left\{ (pNH_3)^r \times (pSO_2)^q \times (pH_2O)^n \right\} = m(1/T + b) \qquad (5)$$

The locus of equation (5) is a straight line when plotted on semi-log coordinates vs. 1/T.

(2) Of the various possible solid products of $SO_2$, ammonia and water reactions, the one determined in a factorial series of experiments to be the principal source of solids in the plume was ammonium bisulfite, ($NH_4HSO_3$) as represented by the following equilibrium relationship:

$$NH_3(vap) + SO_2\ (vap) + H_2O\ (vap) = NH_4HSO_3\ (solid) \qquad (6)$$

Since only one mole of each reacting species is required to produce one mole of solid bisulfite, equation (5) becomes

$$\left\{(pNH_3) \times (pSO_2) \times (pH_2O)\right\} = K_{(Bisulfite)} \qquad (7)$$

Experimental data yielded a numerical relation for $K_{(Bisulfite)}$ in terms of absolute temperature:

$$\log_{10} K_{(Bisulfite)} = -17{,}300/T + 31.4 \qquad (8)$$

Figure 1 shows a plot of $\log_{10} K_{(Bisulfite)}$ versus 1/T. The significance of this graph, summarized, is that any combination of vapor pressures and temperatures representable as a point below the plot of Equation (8) is not conducive to precipitate (fume) formation. (The area beneath this curve is referred to as the "safe zone"). Conversely, operating the scrubber at a point much above the plot of Equation 8 is likely to result in aerosol generation. (This area, consequently, is called the "fume zone".)

Experimental results suggested that the observed appearance and disappearance of aerosols was not as precise as predicted by Equation (8), but actually occurred within a narrow temperature range of about 3° R. This may have been due, in part, to experimental error. To compensate, the abscissa of the plot of equation (8) was shifted to the left a distance approximately equivalent to 3.5°R. This new relationship, shown below and in Figure 1 as Equation (8A), provides a margin of safety against plume formation. (The region in Figure 1 between Equations (8) and (8A) is called the "transition zone".)

$$\log_{10} K_{(Bisulfite)} = -17{,}300/T + 31.24 \qquad (8A)$$

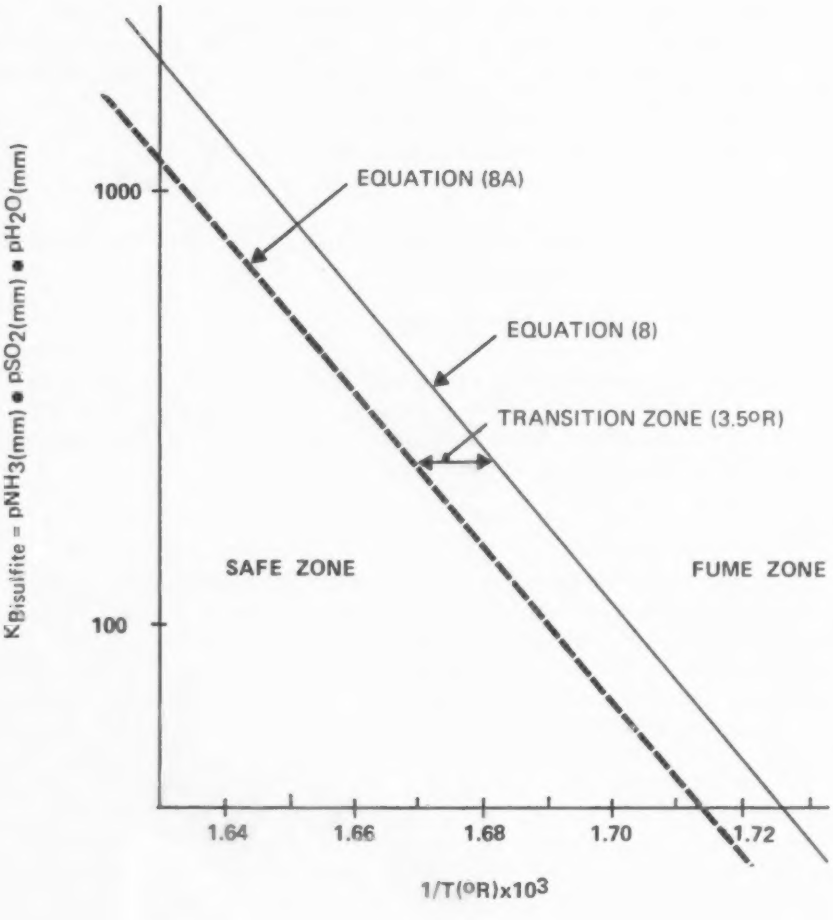
Equations (7) and (8A) contain the essence of the Air Products/Catalytic fume avoidance technology. They are useful for ammoniacal scrubber design when employed in conjunction with reliable $SO_2/NH_3/H_2O$ equilibrium data such as that reported by Johnstone or TVA(13). When applying these equations it is important that the entire absorption system operate totally within the safe zone defined earlier. Care must be taken to avoid local excursions of vapor pressure or temperature into the fume zone. The following situations, for example, should be carefully avoided:

(1) Direct contact of ammoniacal brine droplets with hot, dry gas. (Scrubbing brine should not be admitted to the humidification/cooling chamber.)

(2) Localized cold spots within the absorber. (Insulation of scrubber is normally required to prevent cold regions near the walls.) Cold metal surfaces which conduct heat away from the process fluids should also be avoided. Provision should be made to heat the circulating brine stream during system start-up and at other times when adiabatic conditions cannot be maintained in the scrubber due to cold ambient temperatures.

Figure 1

SUMMARY OF FUME AVOIDANCE CRITERIA



(3) Hot spots in the scrubbing system. This is achieved by initial cooling of the hot flue gas and by avoiding condensation of water vapor upon the entry of flue gas to each scrubbing stage.

(4) Inlet chloride in excess of 10 ppm, which can cause $NH_4Cl$ plume. (The humidification/cooling gas pre-treatment segment should be properly designed for adequate aqueous scrubbing of chlorides.)

(5) Entrained ammonia should be removed from the scrubbed gas prior to discharge through the stack to eliminate the possibility of fume formation outside the scrubber. This can easily be accomplished by subjecting the gas to a slightly acidic water wash followed by effective mist elimination at the scrubber exit. Reheat of clean gas is not necessary to prevent ammonia plumes.

The principles of fumeless scrubbing can best be applied in a multi-stage absorption system employing the "water sandwich" configuration. In this approach, flue gas is contacted with water on both ends of the scrubbing cycle -- initially for humidification and later for ammonia recovery. Contact with ammonia liquor (typically three stages) is sandwiched between the water washes. To reduce the input of ammonia to the final water stage, it is suggested that ammonia feed be metered individually to the desulfurization stages in such a manner that $SO_2$ and ammonia gradients decrease simultaneously on successive stages.

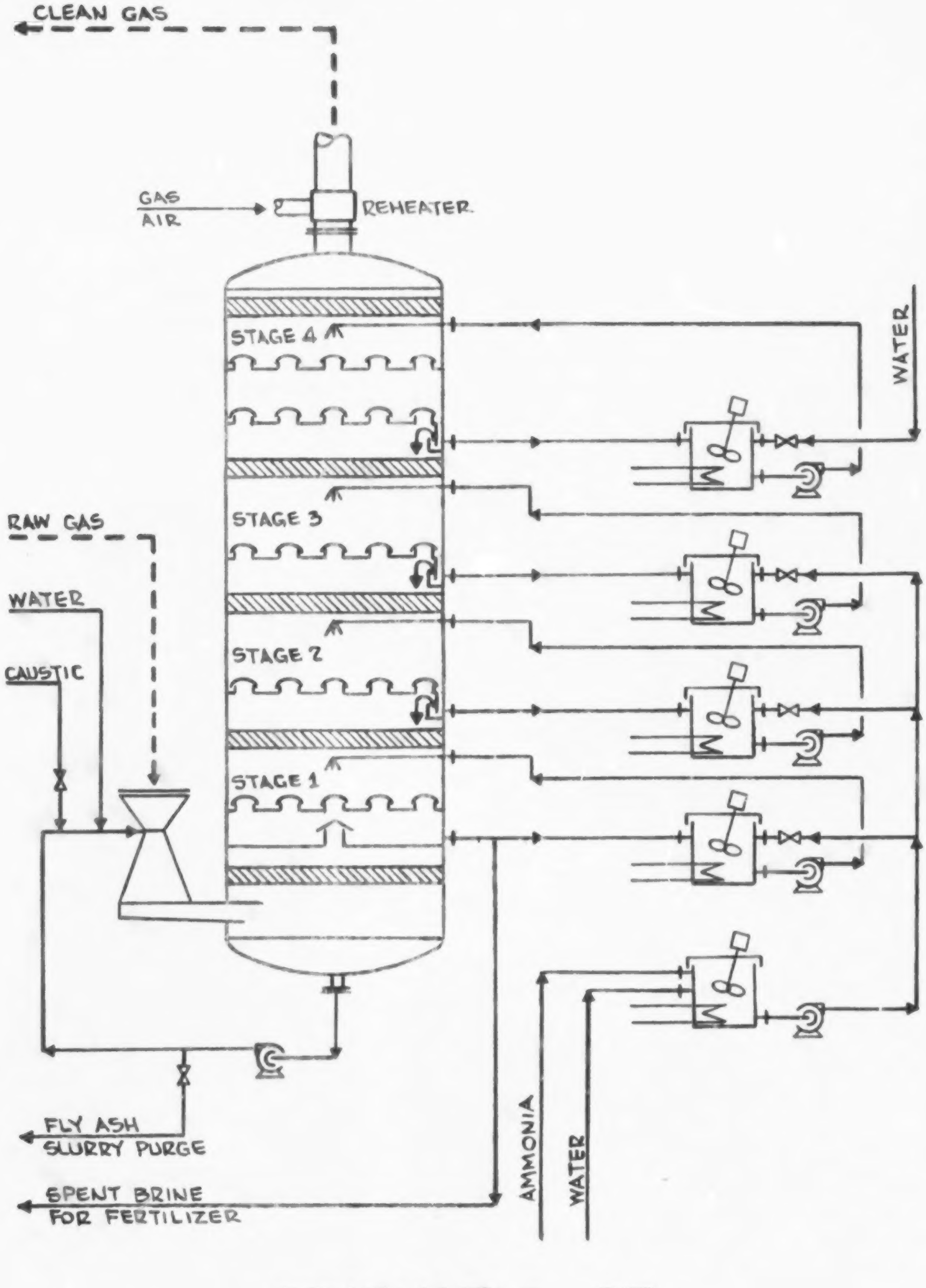
A sample stagewise absorber balance calculated in accordance with the principles outlined above has been published.(9)

## PROCESS DESCRIPTION - CALVERT CITY CASE

A schematic representation of Catalytic's skid-mounted desulfurization unit is presented in Figure 2. A photograph of the equipment installed at Calvert City (showing the absorber tower and gas duct from the host boiler to the scrubbing system) is contained in Figure 3.

### Flow Scheme

Raw flue gas (approximately 4,000 ACFM at 280°F), obtained from a 14-inch diameter tap in the boiler stack, was motivated by a forced-draft blower through a low-energy venturi humidifier, in which the gas was contacted with water and cooled to approach its adiabatic saturation temperature. The venturi also removed some of the fly-ash entering with the gas. Discharge from the venturi entered a four-stage vertical absorber tower, three feet in diameter and 33 feet high, through a sidearm connecting the lower sections of these process units. The base of the absorber contained a mist eliminator (spray-washed) to reduce liquid entrainment followed by a chimney tray to prevent ammonia brine in the stage above from entering the humidification system. A slurry of fly-ash and water was discharged from the tower and recycled to the venturi. A small quantity of caustic was added to the recycle stream for pH control, which effectively improved chloride capture and reduced the potential for corrosion in the venturi loop. A slurry dragstream was bled from the loop and purged. (In a commercial installation, the fly-ash slurry would be further neutralized and thickened prior to purging, but this was not warranted at Calvert City in view of the small quantity of slurry actually discharged.)



SCHEMATIC OF
AMMONIA SCRUBBING PILOT PLANT
FIGURE 2

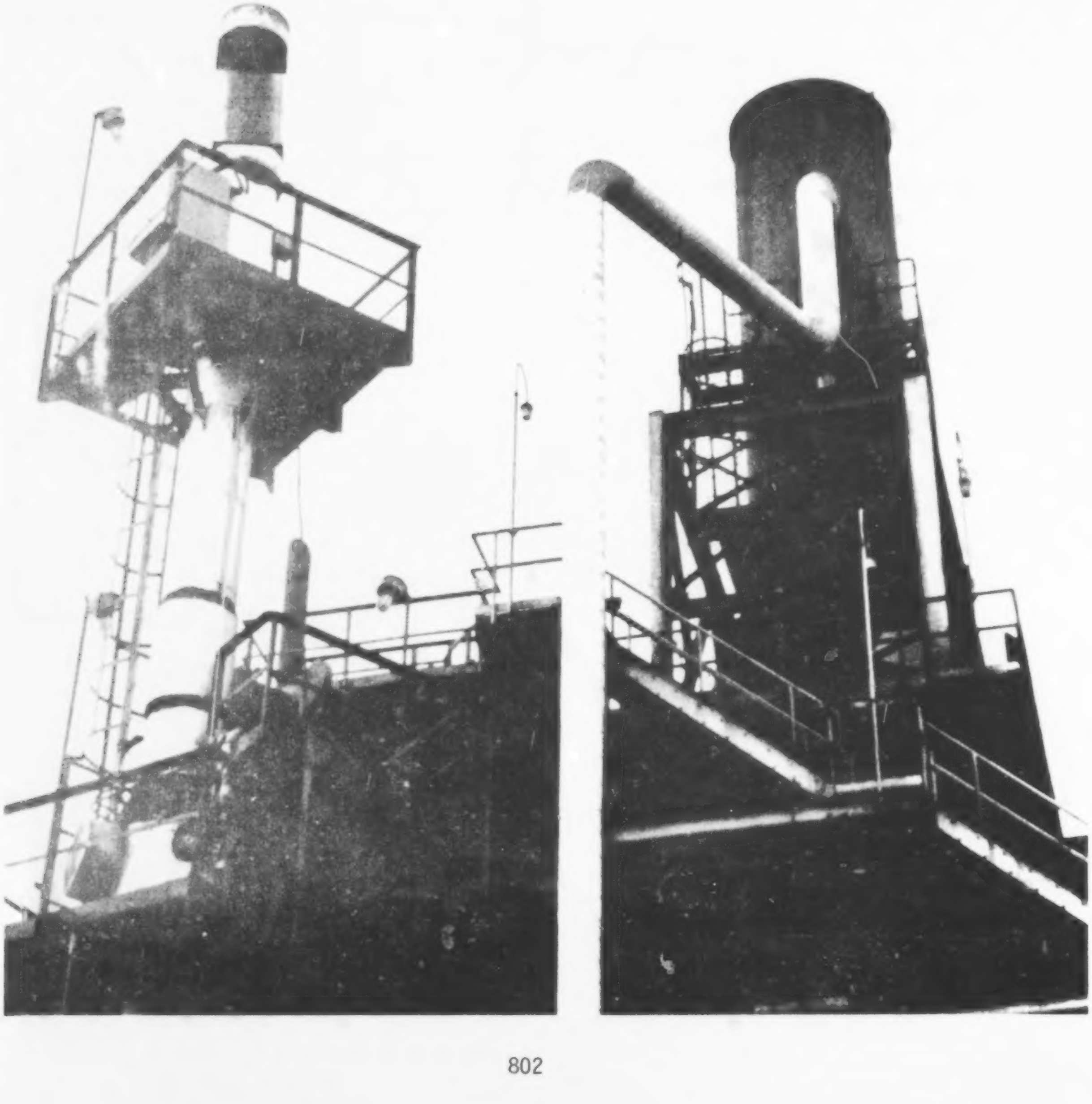


FIGURE 3
Ammonia Scrubbing Pilot Unit
at Calvert City

showing absorber tower (left) and flue gas tap (right)

Stages 1 through 3 of the ammonia absorber each contained one Valve tray, while stage 4 contained two Valve trays. Each of the stages was originally followed by a twelve-inch thick chevron mist eliminator and in a later configuration by a four-inch thick mesh demister. (The mesh units were installed after the chevrons were found to be inadequate, and the chevrons were later removed.) Each stage contained an independent liquor recirculation loop which incorporated a pump and a 370-gallon surge tank fitted with an agitator and a heating/cooling coil. Make-up aqua ammonia was metered by a pH controller to the surge tanks associated with stages 1, 2 and 3. Fresh water was fed to stage 4. Scrubbing liquor passed from stage to stage by means of overflow weirs integrated with the tray downcomers. On each stage, the liquor recirculation rate was much higher than the rate of overflow to the next lower stage.

Spent brine from stage 1 was pumped to a storage drum, from which it was ultimately removed from the site by an agricultural chemical dealer's tank truck.

The molar ratio of $SO_2$ to ammonia was controlled on each stage so that the concentrations of both species decreased on successively higher stages. On stage 4, residual ammonia was captured in a recirculating water wash. A small amount of $SO_2$ was, of course, also absorbed in this wash solution, which maintained its pH slightly on the acid side and increased its affinity for $NH_3$.

Flue gas leaving stage 4 was reheated by a direct-fired gas burner prior to discharge through a 20-foot stack mounted above the absorber. An in-line opacity meter was stack-mounted an appropriate distance above the reheater.

### Typical Operating Parameters

Operating conditions were varied throughout the program for experimental purposes. Following is a summary of typical operating conditions which might be appropriate for "routine" operation at Calvert City:

| | | |
|---|---|---|
| Inlet Gas | Flow: | 4,000 ACFM @ 280°F |
| | $SO_2$ Input: | 1,600 ppm |
| Water Circulation | Venturi Loop: | 100 gpm |
| | Scrubber State Loops: | 40 gpm |
| By-Products | Spent Ammonia Brine: | 2 gpm |
| | Fly-Ash Purge: | <1 gpm |
| Operating Pressures | Venturi: | 6 inches WC |
| | Total System (inlet duct thru stack): | 28 inches WC |

### Materials of Construction

Following is a summary of materials of construction employed for equipment items. A discussion of the performance of these materials is presented later.

| Item | Material |
|---|---|
| Venturi Humidifier/Cooler | Carpenter Alloy 20 CB-3 |
| Ammonia Absorber | |
| Shell (insulated) | FRP lined carbon steel |
| Trays (stages 1, 2, 3) | Stainless steel 316-L |
| Trays (stage 4) | Hastelloy "G" |
| Mist Eliminators (chevrons) | Noryl Plastic |
| Mist Eliminators (mesh pads 1,2,3) | Stainless Steel 316-L |
| Mist Eliminator (mesh pad 4) | Polypropylene |
| Pump (venturi loop) | Rubber lined |
| Pump (stage loops 1,2,3) | Stainless steel 316-L |
| Pump (stage loop 4) | BUNA-N lined |

### Analyses

The following principal analyses were routinely made on each absorber stage:

- $SO_2$ (analyzer-recorder)
- pH (analyzer-controller-recorder)
- Specific gravity (grab sample - lab analysis)
- Temperature (sensor-recorder)
- Sulfite/sulfate (grab sample - lab analysis)

The following principal analyses were routinely made in the gas exit stack:

- $SO_2$ (analyzer-recorder)
- Opacity (monitor-recorder)
- Temperature (sensor-recorder)

### Control Philosophy

Preset $SO_2$-to-ammonia mole ratios were maintained by independent pH controllers on stages 1, 2 and 3, which regulated ammonia input to these stages.

Absolute ammonia concentration was determined from pH measurements coupled with specific gravity laboratory analyses. Adjustments in water input to the scrubber were made when necessary. An ammonia analyzer was installed, but it was frequently out of service due to sampling problems. With daily maintenance, this instrument was ultimately used with some success during the latter part of the program.

Stagewise temperature control was available, but not used. Operation proceeded without temperature adjustments.

## DISCUSSION

To summarize the Calvert City program simply in terms of "success" or "failure" would be a gross oversimplification of the relevant facts. On the one hand, experimental limitations imposed primarily by continuous (but non-uniform) fly-ash intrusion and compounded by spotty equipment and instrument performance made it impossible to characterize the feed gas or to complete detailed material balances around the absorption system. This, in turn, impeded efforts to complete the rigorous optimization studies originally contemplated. On the other hand, Catalytic's adaptation of what was essentially a bench-scale technology to the capricious flue gas from a coal-fired boiler was successfully accomplished in a relatively short time. Historical evidence suggests that merely correcting mechanical problems and developing a workable interface with the host boiler has often taken process developers longer than the six months which was allocated for Catalytic's entire program.

The results obtained at Calvert City were essentially qualitative. Taken alone, they do not establish beyond doubt the validity of the fumeless scrubbing criteria. They do, however, reflect positively on overall process viability and generally tend to confirm the results of earlier studies.

## Fume Formation

The only indisputable proof of fumeless scrubbing would have been consistent scrubber operation with a completely clear stack. Unfortunately, in all runs (including those conducted without ammonia) some smoke was detected by a stack-mounted opacity meter even though it was not always optically visible. A series of runs in which non-fuming caustic lye was substituted for ammonia and the steam plume was eliminated by reheat revealed a base opacity ranging from roughly 2% to 7%. Specific measurements made on three successive days were as follows:

| Opacity % | Date |
|---|---|
| 3 ± 1% | 31 May |
| 6 ± 1% | 1 June |
| 6 ± 1% | 2 June |

Occasionally during the ammonia studies opacities as low as 3% to 4% were recorded. The best sustained and reproduceable operation at Calvert City, using ammonia, was about 10% opacity while scrubbing 90% of the incumbent $SO_2$. It should be noted that the effective path length of the opacity sensor as installed was approximately 50 inches. This distance is roughly equivalent to the diameter of a 15-megawatt boiler stack.

The following should be noted about particulate fumes observed at Calvert City:

(1) During test runs with and without ammonia, plumes leaving the scrubber appeared to contain a bluish component. In addition, a blue fringe could occasionally be observed around the plume generated at the main boiler stack.

(2) Particulate fumes typically observed at Calvert City when scrubbing in the fumeless mode were not at all persistent and were much less obvious than the dense fumes commonly associated with ammonia scrubbing. It was possible, however, to generate dense fumes at Calvert City "on cue" by deliberately violating the fume avoidance criteria.

Two things are clear based on these observations:

(1) A bluish tinge does not necessarily signal the presence of ammonium salts in a plume. The observed color depends upon the wavelength of light reflected by the particles comprising the plume which itself is a function of their size and uniformity.

(2) Application of the fume avoidance criteria at Calvert City resulted in a marked reduction in stack opacity from what has historically been noted in conventional ammonia scrubbing operations.

In Catalytic's judgment, the Calvert City results (particularly when compared with parallel laboratory studies) strongly suggest that the particulate emissions from the pilot plant stack consisted of fine fly-ash, and that the scrubber was controllable with respect to ammonia fume generation.

## Equipment Performance

Forced Draft Blower: Instability in the skid-mounting of the blower caused excessive vibration during initial testing. The problem was rectified by anchoring the unit with bolts imbedded in a concrete foundation of sufficient mass. It was also found that condensation of the inlet gas was responsible for the accumulation of solids and liquids within the blower, which increased the vibrations. This problem was solved by (1) insulating the gas inlet duct leading to the blower to reduce condensation, and (2) adding a valved casing drain to the system. Little pitting was observed on the carbon steel blower wheel.

Venturi Humidifier/Cooler: Pressure drop in the venturi could be varied by raising or lowering a conical throat plug. The manufacturer guaranteed 100% humidification of the inlet gas at 6 inches w.c. pressure drop and a water circulation rate of 100 gpm; consequently, these parameters were selected for normal system operation. The degree of compliance with the guarantee was not precisely evaluated since outlet gas humidity and particulate loading could not be measured. Actual performance, however, appeared to be satisfactory. Theoretically, the venturi could have been operated at higher energy levels to compensate for the lack of an electrostatic precipitator. In practice, the blower could not provide sufficient motivating force, so venturi operation was limited to the 4-to-8 inch w.c. range.

The venturi operated well even when the recirculating water stream contained more than 10% suspended fly-ash. The radial, 1-inch inlets tended to plug during periods of continuously high solids loading.

Very little pitting of the Carpenter 20-CB3 unit was evident on inspection, but mirror-polish of venturi internals and rounding of sharp edges on test coupons provided evidence of abrasion.

A venturi was selected for gas humidification (rather than a less costly spray chamber) due to the manufacturer's claim that the venturi would eliminate a wet/dry interface near the gas inlet and therefore reduce the potential for accumulation of a fly-ash cake in that area. The venturi was found to be entirely satisfactory in this regard.

Ammonia Absorber Tower: The carbon steel tower shell was lined with Heil Rigiline 413G, an epoxy-based, fiberglass-reinforced resin, trowel-applied to a thickness of 1/8 inch. Because of limited accessibility to the numerous support rings and bolting strips welded inside the three-foot diameter column, small sections of the lining were not properly applied and corrosion of the metal tower shell promptly developed. Repairs resulted in about six weeks' loss in operating time; but, once the corroded areas had been properly sandblasted and relined with the same resin, no further shell corrosion was encountered. Although the use of a lined tower might be ideal for a commercial installation, it was found to severely restrict the flexibility of pilot operations. For example, ordinarily simple projects such as flange-mating, nozzle or tap addition, manway closure and internal tray sealing all required major efforts.

Absorber Tower Internals: The five installed valve trays ultimately performed well, but some difficulty with leakage was encountered early in the program. As indicated above, the tower lining made installation, sealing and servicing of the trays more difficult and time-consuming than anticipated. Again, these kinds of problems were magnified by the restrictive diameters of the tower (3 ft.) and the manways (18 inches). Such difficulties are avoidable in commercial-size systems.

No corrosion problems were noted on inspection of the three stainless steel 316L trays (pH exposure 5.5 to 6.5) or the two Hastelloy "G" trays (pH exposure as low as 1.8 but more typically around 3).

The absorption system was originally fitted with five chevron mist eliminators, positioned as shown in Figure 2. The originally installed set was too small and channeling occurred around the edges. A replacement set was hard to install due to the tower lining, and once in place, the chevrons did not perform satisfactorily. Constructed of Noryl plastic, they tended to deform above approximately 150°F. After extended service, a tendency toward brittleness was noted. For proper operation, a distance of 1-1/4 inches should have been maintained between the blades. This was difficult to accomplish in the circular column.

Mesh-type mist eliminators, 4 inches thick, were installed above the chevrons to reduce liquid entrainment. These performed satisfactorily; but a shrinkage of the mesh pads was observed after extended service.

Chimney Tray: Positioned near the bottom of the absorber tower, the chimney tray originally contained a single, 8-inch by 20-inch rectangular chimney, 6 inches tall, covered by a flat "hat" mounted three inches above the chimney lip. During start-up it was found that the distribution of gas leaving the chimney was so uneven as to cause severe malfunction of the valve tray directly above ("blowing" of one side of the tray and excessive liquor weepage from the other side). This problem was alleviated to an acceptable extent by raising the "hat" to nine inches above the chimney.

No corrosion of the Hastelloy "C" tray was noted, even though its underside was exposed to highly acidic liquor which contained chlorides.

Pumps: The closed-impeller stainless steel 316-L centrifugal pumps installed in stage loops 1, 2 and 3 provided highly satisfactory, trouble-free performance. Routine gland repacking and removal of caulking from the impeller area were the only maintenance requirements. Performance of the rubber-lined pump in stage loop 4, however, was inadequate. The natural rubber liner swelled excessively and and was replaced with one made of BUNA-N. Frequent realignment of the pump was required.

The venturi loop pump was also rubber-lined. Its performance was consistently excellent. No maintenance was required.

Piping - Humidification Loop: FRP piping performed well except for bends near the venturi inlet, which were subject to high abrasion.

Piping - Ammonia Brine: Rubber hoses fitted with quick-disconnect joints proved leakfree and highly flexible. Some pitting was observed on stainless steel inserts.

Ductwork: The carbon steel inlet gas tap did not corrode in service, except for a 2-foot section adjacent to the venturi, which was subject to acidic backsplash. This section was replaced with stainless steel 316.

## Instrument Performance

### $SO_2$ Analyzer

Analysis of gas-phase sulfur-dioxide proved to be the most frustrating instrument problem encountered. The $SO_2$ analyzer and its associated sampling system was the most expensive instrument item in the test unit. Making it work was, in itself, a major development program. Most component systems of the analyzer presented problems. For example, the sampling probes could not deliver liquid-free samples until tubular baffles were installed, thus shielding the probes from direct liquid impingement. In addition, a number of carbon steel fittings in the probe assemblies quickly corroded and were replaced with new ones of CPVC. The sample tubing (teflon) was subject to leaks and occasional plugging. Solenoid valves associated with the sample manifold were subject to corrosion and leaks. Replacement with electrically activated SS-316 ball valves mounted in a thermostatically controlled environment was required. The sample pump, probably oversized, aggravated the entrained liquid problem described above by sucking condensate through the sample filter. Gradually, these and other problems were resolved, but not without significant effort.

The analyzer itself, containing and electrochemical transducer, performed well. Nevertheless, reliable integral operation of the instrument package was not realized until only four weeks before final shutdown of the plant. The lack of reliable $SO_2$ concentration data for about five months reduced the Calvert City program to essentially a qualitative study.

### Opacity Meter

Reheated flue gas opacity was continuously monitored by an emissions monitor. Unexpected drift was encountered and twice-daily manual recalibration was required. The instrument reading was affected by incidental sunlight on the stack. To alleviate this problem, an offset stack extension was installed which provided some degree of shade. The offset can be seen in Figure 3.

### Gas Flow Measurement

Flue gas flow rates into the absorber were measured with an annubar (which is a flow-averaging pitot tube). Incoming fly-ash particles tended to coat the annubar orifices and distort the flow measurements. In addition, the annubar was improperly installed -- there were too few pipe diameters upstream and downstream of the sensor, which made all gas-side flow measurements uncertain. To reduce the particulate interference problem, an intermittent 150-psig air purge was installed. However, if additional studies are conducted, the annubar will be replaced by a different kind of instrument -- for example, one based on the principle of heat conduction from a hot wire immersed in the gas stream.

### pH Measurement

Ammonia addition to the various absorber stages was controlled by pH which was measured by Uniloc Model 1200-V meters. The electrodes were housed in a Uniloc Model 320 sensor assembly. Trouble-free performance was experienced, even at moderate fly-ash loadings in the brine. Double-junction electrodes were required, however, to prevent drift.

### Ammonia Measurement

A specific-ion sensor, containing an ammonia gas sensing electrode, was utilized to measure the ammonia content of brine leaving the absorber. The electrode itself performed well, but the sampling system, which contained peristaltic pumps (i.e., pumps inducing successive compressive waves in a flexible conduit) was inadequate. Life of the silicone peristaltic conduit averaged less than one week. Small (1/16 inch) diameter connective tubing was highly susceptible to plugging. Despite exemplary field service by the manufacturer, reliability of the sampling system could not be improved.

Presently, there is no adequate replacement for this device in dirty gas service that is conducive to fully automatic scrubber operation. Short-term expedients at Calvert City involved installation of a cartridge filter plus daily replacement of tubing. For experimental purposes, laboratory analyses of grab samples provided necessary operating data.

The foregoing is a summary of observations made at Calvert City which hopefully conveys an accurate overall impression of the test program: tedious work ultimately resulting in measurable progress toward solving problems associated with field-testing a stack gas scrubber. Even though Catalytic's initial objective of developing an optimization data package within six months of start-up was, in retrospect, too ambitious, the program as completed did generate the following conclusions:

## CONCLUSIONS

1. The test unit operated with extremely high availability despite significant variations in inlet gas composition and particulate loading. After initial (non-recurring) problems were rectified, extended operation with only routine maintenance was demonstrated. No plugging or scaling was experienced.

2. The ability to remove 85 to 90% of $SO_2$ from incoming flue gas while discharging cleaned gas having a total opacity in the 10% range was demonstrated. Inlet $SO_2$ was approximately 1,500 ppm while background (fly-ash) opacity was conservatively estimated at 6%. Spent scrubbing brine (fertilizer) containing 6 moles of ammonia per 100 moles of water was by-produced.

3. Operation by automatic control was demonstrated with one operator per shift. The unit adjusted well to inlet $SO_2$ fluctuations.

4. The ability to operate the absorber and the venturi with unusually heavy particulate loading (upset boiler conditions) for short periods of time was demonstrated. Similarly, the ability of these units to operate under moderately dirty conditions for extended periods was established. The absorption unit tended to be self-cleaning after inlet fly-ash was reduced to normal levels.

5. The ability of the venturi and absorber working in series to remove a significant fraction of inlet fly-ash was established.

6. A complete equipment and instrument list was established. Materials of construction for major equipment items were verified.

7. Relatively simple start-up and shutdown procedures were established.

8. The suitability of valve trays for desulfurization by aqueous ammonia was established. These trays are capable of operation in dirty service, as indicated in point (1).

9. The effectiveness of mesh demisters for entrainment reduction (and maintenance of sharp concentration profiles in the column) was established.

Even though much has been learned at Calvert City, several objectives remain to be accomplished. The following would be priority items if Catalytic's optimization program were to proceed to the next stage:

1. Installation of fly-ash control system and demonstration of clear-stack operation.

2. Completion of detailed material and energy balances around the absorption system.

3. Establishment of "optimum" operating conditions.

4. Improvement in the procedure for continuous liquid-phase ammonia analysis.

## NOMENCLATURE

| | |
|---|---|
| b,m | Constants defining the intercept and slope, respectively, of the log-log plot of Equation (5) |
| $K_{Bisulfite}$ | Product of the partial pressures of $NH_3$, $SO_2$ and $H_2O$, as defined in Equation (7) |
| n,q,r | Number of moles of reacting $NH_3$,$SO_2$ and $H_2O$, respectively |
| $pNH_3$, $pSO_2$, $pH_2O$ | Vapor pressures of $NH_3$, $SO_2$ and $H_2O$, respectively, expressed in millimeters of mercury |
| T | Absolute temperature, degrees Ranline |

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## APPENDIX - PROCESS ECONOMICS

A schematic flow diagram of the integrated Catalytic/IFP/CEC process for simultaneous removal of $SO_2$ and $NO_x$ with recovery of elemental sulfur is presented in Figure 4. Two preliminary cost estimates are considered below: Case I encompasses all of the operations shown in the Figure, while Case II represents a simpler process without $NO_x$ removal capability. In both cases, reducing gas for sulfur production is generated by coal gasification.

Process options which involve the recovery of part or all of the spent ammoniacal brine as fertilizer or commercial grade ammonium sulfate are available. Information relating to the applicability and cost of these alternative systems is available on request.

### Estimating Bases

The following was assumed in developing the preliminary economics presented below:

- New, 500-MW utility boiler firing 3.5% sulfur coal and fitted with an efficient, conventional electrostatic precipitator.
- 90% $SO_2$ removal will be achieved.
- 80% $NO_x$ removal will be achieved (Case I only).
- Stack Gas reheat is not included, based on steam plume acceptability.
- The unit will operate the equivalent of 7000 hours per year at essentially full load.

### Capital Investment

The estimates presented in Table 1 have been reckoned on a turnkey basis. It is assumed that work would begin at a clear, level site and that all necessary services would be provided to deliver a completed gas scrubbing facility. Battery limits are assumed to extend from the precipitator exit flange to the stack inlet flange.

A 500-MW installation would normally include three ammonia absorption modules, two IFP-sulfur recovery modules and two CEC-$NO_x$ control modules. A system of this type can efficiently follow a boiler load ranging periodically from 100 to 550 MW.

Plant investment for fumeless, regenerable ammonia scrubbing is about $132 per KW for Case I and $96 per KW in Case II. Total Capital Investment is roughly 20% higher for both cases, as shown in Table 1.

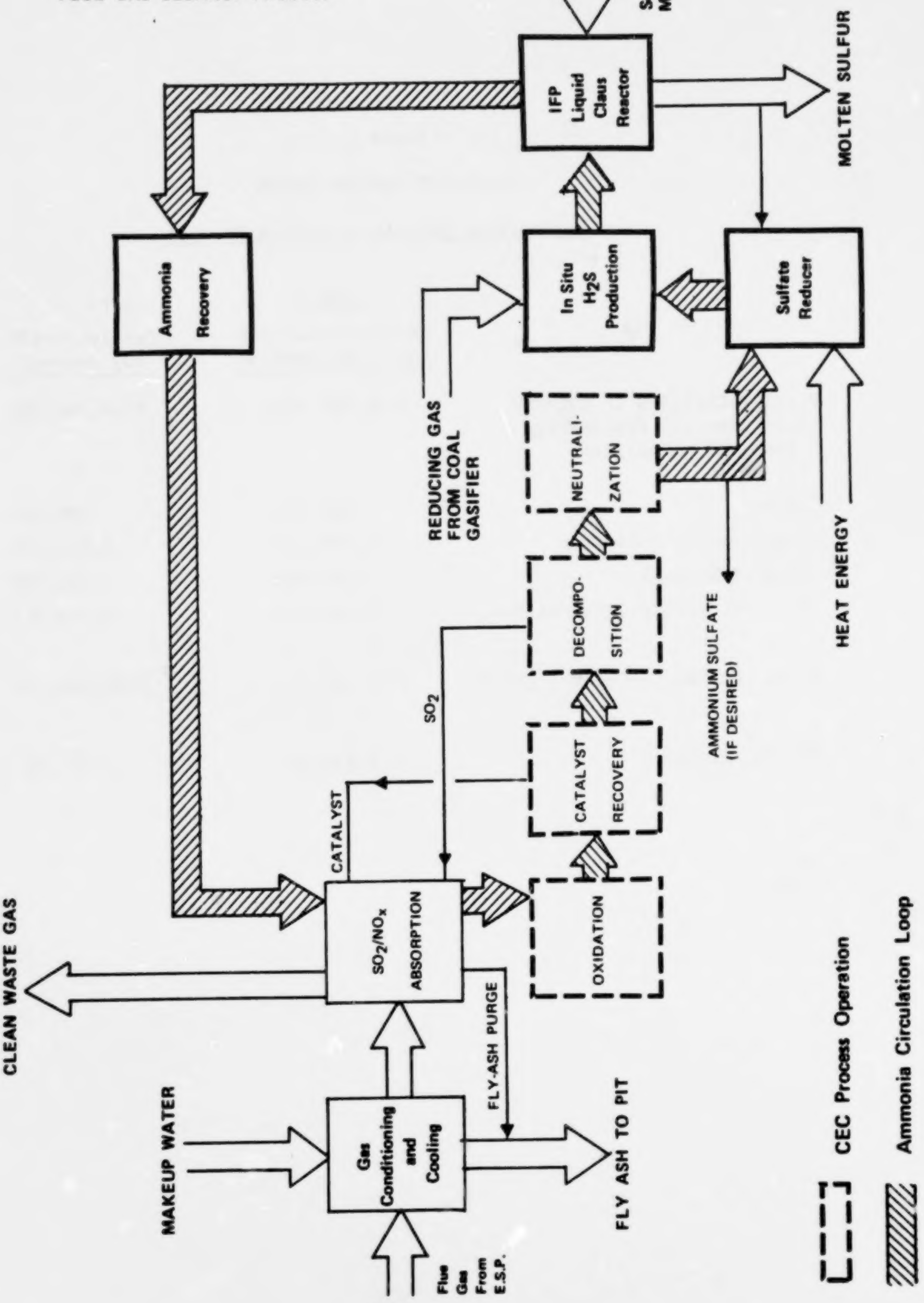
### Operating Costs

A summary of operating costs is presented in Table 2. The following unit costs were assumed:

| | | |
|---|---|---|
| Electricity | $ 0.025 | per KWH |
| Steam | 2.50 | per thousand pounds |
| Coal (bituminous) | 20.00 | per ton |
| Ammonia | 140.00 | per ton |
| Abatement Sulfur | 50.00 | per ton |

It should be noted that the Annual Revenue Required in Case II (with by-product credits) compares favorably with recently published figures for limestone processes.

## Figure 4
## CATALYTIC-IFP-CEC FLUE GAS CLEANUP PROCESS



## TABLE 1

## ESTIMATED CAPITAL COSTS

## Regenerable Ammonia Scrubbing Process

| | CASE I<br>Catalytic-CEC-IFP<br>$SO_2$ & $NO_x$ Removal | Case II<br>Catalytic-IFP<br>$SO_2$ Removal |
|---|---|---|
| PLANT FACILITIES INVESTMENT (Includes all applicable fees and royalties) | $ 66,000,000 | $ 48,000,000 |
| Land | 100,000 | 100,000 |
| Organization & Startup | 4,500,000 | 3,300,000 |
| Working Capital | 1,500,000 | 1,400,000 |
| Interest during Construction | 8,000,000 | 6,000,000 |
| TOTAL CAPITAL INVESTMENT (TCI) | $ 80,100,000 | $ 58,800,000 |
| TCI PER KILOWATT | $ 160.20 | $ 117.60 |

## TABLE 2
## ESTIMATED ANNUAL OPERATING COSTS
### Regenerable Ammonia Scrubbing Technology

| | Case I<br>Catalytic-CEC-IFP<br>$SO_2$ & $NO_x$ Removal<br>(millions of dollars/yr) | Case II<br>Catalytic-IFP<br>$SO_2$ Removal<br>(millions of dollars/yr) |
|---|---|---|
| **Variable Costs** | | |
| Utilities & Chemicals | 4.15 | 1.83 |
| Coal (for reducing gas) | 2.24 | 1.49 |
| Petroleum Distillates & Natural Gas | None | None |
| **Fixed Costs** | | |
| Maintenance (Material & Labor) | 2.99 | 2.25 |
| Other Labor Categories (including Payroll Burden) | 1.22 | 1.06 |
| General/Administrative Expenses | 1.49 | 1.13 |
| Property Taxes & Insurance | 1.49 | 1.13 |
| Depreciation | 2.97 | 2.24 |
| **Annual Operating Cost** | 16.55 | 11.13 |
| Interest<br>Return on Investment<br>Income Tax | 7.36 | 5.58 |
| By-product Credits | (2.80) | (2.07) |
| **Annual Revenue Required** | 21.11 | 14.64 |
| (mills per KWH) | 6.03 | 4.18 |

# ADVANCED PROCESSES SESSION

Session Chairman

**Kurt E. Yeager**
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# ADVANCED FGD PROCESSES

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# SYMPOSIUM ON FLUE GAS DESULFURIZATION

## Advanced FGD Processes

11/11/77

Kurt E. Yeager

### Introduction

Although this session is entitled "Advanced Processes," a more accurate title might be "Advanced Applications and System Improvements." Our focus is less the development of new process options than the application of relatively established processes and sub-processes in more efficient system combinations. The objective of these new combinations is either to reduce the cost of existing flue gas desulfurization processes, create more acceptable byproducts or reduce operating problems and inefficiencies.

This approach, which places priority on reducing the impact of flue gas desulfurization on the using industry, and the consumer, is driven by economic reality. Between now and the period 1985-1990, coal-fired utility generating capacity is committed to expand by 120,000 MWe. This will involve 250 units consuming 360 million tons of coal annually. This will nearly double the current utility coal-fired generating capacity. Because of the preliminary development status of alternative coal combustion and conversion technology, all of this capacity will be in the form of current pulverized coal combustion systems plus auxiliary environmental control technology. The economic impact of the 1977 Clean Air Act Amendments, depending on the outcome of judicial and political interpretation, will substantially increase the costs of these new, pulverized coal generating units. It is estimated, for example, that the average capital cost penalty for control of all pollutants will be 40% ($250-300/kw) of new unit costs and the operating and maintenance cost penalty will be about 100% (12 mills/Kwhr) and the heat rate penalty 15%. On a utility industry-wide scale, these requirements convert to a capital investment of $60 billion, not including interest, $1 billion in additional operating costs annually and 50 million tons per year additional coal consumption in the 1985-1990 time period. Thus, the cost savings to the electricity consumer through even small reductions in the cost and inefficiency of environmental control technology are in the billion dollar category.

The issue of whether flue gas desulfurization technology meets the environmental improvement objectives for which it is intended, is debateable. On the other hand, there are no superior or even available alternatives that can be commercially considered over at least the next 10 years. It is also clear that value judgement on FGD use will not be affected by efforts to marginally reduce the cost and inefficiency of this technology. Users, suppliers and government must work together and demonstrate a "best effort" to minimize technical risk and cost. Public utility commissions are making it clear that such an effort will be necessary if they are to be able to pass on the costs of "Best Available Control Technology" (BACT). If the utility cannot recover these costs through the rate base, it cannot acquire capital for either system expansion or environmental control. Thus a cooperative technical effort among users, suppliers and government is being established to provide a sufficient R&D resource pool for minimizing the substantial impact of this environmental control technology. This session is intended to indicate the direction of this emerging joint effort, dedicated ultimately to the electricity consumer, and encourage increased emphasis on the value of these approaches to all concerned.

# SUBSYSTEM COMBINATIONS FOR RECOVERY PROCESSES ADDRESSING THE PROBLEMS

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## ABSTRACT

Hybrid process and subsystem combinations may reduce the cost of existing flue gas desulfurization processes, create more acceptable byproducts, or eliminate operating problems. Specific subsystem requirements to achieve these objectives include sodium-sulfur compound reduction, direct reduction of $SO_2$ to sulfur, novel absorption or contactor designs, and subsystems for retrofitting existing lime/limestone scrubbers to eliminate sludge production. Examples of subsystems with potential to respond to these requirements include the following: (1) sodium sulfate reduction (molten bath) to eliminate sodium purge for dry sorbent regeneration, and for sodium throwaway or dual alkali byproduct conversion to sulfur; (2) modified aqueous scrubbing with steam stripping to produce concentrated $SO_2$; (3) direct $SO_2$ reduction to sulfur with coal for use on $SO_2$ concentrating processes; (4) acid sulfate absorption for lime/limestone system retrofit to produce gypsum using limestone as feed.

A summary of the (preliminary) cost potential for hybrid systems including steam stripping/direct reduction, char absorption/direct reduction, and dry injection plus molten bath regeneration is also presented.

# SUBSYSTEM COMBINATION FOR RECOVERY PROCESSES
# ADDRESSING THE PROBLEMS

The use of advanced systems or concepts in Flue Gas Desulfurization (FGD) is this sessions topic. This paper will address special problems in FGD, and subsystems or novel concepts that may solve some of these problems. System cost and complexity, reactant availability, by-product quality and type are major utility concerns addressed in this paper.

## Problems

Problems with FGD that must be faced by the utility industry include reducing solid and liquid disposal impact, encouraging use of available reactants and minimizing use of scarce energy sources.

Most current lime/limestone systems operating on eastern coal produce a calcium sulfite/sulfate sludge that is ponded or landfilled. Sulfite ion is an oxygen scavenger and leaching or runoff from ponds can cause high local C.O.D. in surface or ground water. Sulfite/sulfate mixes are often thixotropic and will liquefy when agitated, making them unsuitable for landfill in an unstabilized or unfixed form. Sodium compound disposal is even more difficult since sodium compounds are soluble and sodium sulfite is a commonly used oxygen scavenger. Pond linings to prevent groundwater contamination are expensive, and tend to develop slow leaks with time.

Natural gas used as a reductant in FGD processes is becoming less available and lime cost is expected to rise with the cost of energy.

## Solutions Needed

To solve the problems mentioned above, utilities need to be able to produce usable/disposable by products such as sulfur, sulfuric acid, concentrated $SO_2$, or gypsum, utilizing common reactants like coal and limestone in simple and reliable contactor designs or scrubber subloops. Additionally they need the ability to reduce spent sodium/sulfur compounds and produce elemental sulfur.

## Subsystems Which Meet These Needs

There are subsystems which address these utility industry needs. These subsystems are not always marketed individually, and not always proposed in the suggested combinations. In this paper general subsystems are suggested and specific processes are addressed in more detail.

Examples of subsystems include concentrated $SO_2$ reduction without use of reducing gas (Foster Wheeler Energy Corp RESOX(TM), Modified Allied Chemical); aqueous absorption with indirect steam heat $SO_2$ stripping (Peabody Engineered Systems, Spring Chemical Corp); sodium sulfate reduction to eliminate sulfate purge, for dry sorbent regeneration and for sodium scrubbing or dual alkali retrofit (TSK, Atomics International); new contractor development to improve existing lime/limestone processes (co-current contactor and Chiyoda 121 jet bubbling reactor); acid sulfate absorption for lime/ limestone system retrofit to produce gypsum using limestone as feed (DOWA).

A prime result of EPRI's Regenerable Flue Gas Desulfurization Process evaluation to date has been to highlight the need for workable subsystems which reduce the complexity and cost of sulfur production.

## Reducing $SO_2$ To Sulfur

An example of utility concern is with systems using reducing gas to produce sulfur. This is discussed in detail in the upcoming paper by Milt Beychock and Archie Slack (1). The historic way to make $H_2$ or CO for reduction is to reform natural gas or light hydrocarbon liquids such as naphtha. Several system combinations have been suggested in a recent paper by Battelle. The Allied process has been utilizing natural gas directly with concentrated $SO_2$ to form elemental sulfur. While this eliminates several steps, it still depends on natural gas - and its availibility is being limited.

Gasification processes can utilize coal, but are complex chemical processes in themselves and many utilities do not wish to add to their problem by operating the current generation of gasifiers. The reducing gas may not need extensive cleanup compared to SNG production, but it still would require tar removal and this could cause a water pollution problem. Some gasifiers (Lurgi) require pressurization, lock hoppers, tar removal, and still others (Koppers-Totzek) operate at slagging temperatures requiring an oxygen stream that would have to be produced nearby. Due to the large volumes of explosive gas in some systems, inerting/purge equipment and explosion proof controls must be provided. Many systems generate $H_2S$ and are pressurized, causing concerns about safety hazards in enclosures. While none of these individual concerns would in itself preclude gasification it does make utilities cautious, and causes them to seek other ways of using the available reductant, coal.

Developing a subsystem to reduce $SO_2$ to elemental sulfur without reducing gas is therefore a goal of EPRI's $SO_x$ subprogram. We are funding development of a 42 MW size RESOX$^{(TM)}$ reactor in Lünen, West Germany in an effort to meet this goal. This testing will be sponsored by EPRI and a consortium including Foster Wheeler Energy Corporation, STEAG, Deutsche Babcock and Bergbau Forschung with program cost sharing by the German government agency Umsweltbundesambt.

The RESOX process reacts $SO_2$ with crushed coal in an atmospheric, temperature controlled vessel at 1400°F causing the overall reaction $SO_2 + C \quad CO_2 + S$. Sulfur, unconverted $SO_2$ and unreacted carbon are the primary products. The unreacted carbon from the coal can be ground and fired in conventional boilers. The unconverted $SO_2$ can be recycled to the absorber inlet. Gaseous sulfur can be condensed and either sold as liquid or stockpiled as solid depending on purity level and local market.

Examples of processes that should be easily capable of combining with the subsystem are Wellman-Lord, Bergbau-Forschung, and Absorption/steam stripping. Examples of processes with less usable $SO_2$ rich gas streams include magnesia slurry scrubbing and high pH ammonia scrubbing.

Easily combined systems such as Wellman-Lord, Bergbau-Forschung and Absorption/steam stripping have concentrated $SO_2$ outputs and little contamination. The Wellman-Lord and Absorption/steam stripping process make primarily $SO_2$ with some $H_2O$. Overhead $H_2O$ condenser conditions in steam stripping can vary the amount of water left in the $SO_2$ stream to match RESOX needs more exactly. A 20%-40% $SO_2$ stream seems to be preferred with the balance $H_2O$ and inert gas such as nitrogen. Bergbau-Forschung has been proposed with RESOX use for some time and the combined concept will be evaluated on the 42 MW scale in Germany at Lünen.

In the case of magnesia slurry scrubbing, the $SO_2$ stream is dilute and has a high oxygen content. Not only is the magnesium oxide dust a contaminant to the sulfur or spent coal product, but the high $O_2$/dilute $SO_2$ gases will consume excess carbon to form carbon dioxide and cause the percent $SO_2$ conversion to drop. This in turn may cause excessive recycle and higher operating costs. EPRI does intend to investigate the oxygen limits by simulating this magnesia off-gas on RESOX both at lab scale and at Lünen 42 MW scale.

High pH ammonia solutions can be stripped of $SO_2$ by heating, but may evolve ammonia as well as $SO_2$ and, in conjunction with RESOX, there is potential for ammonia breakthrough, fume formation and cyanide production. Obvious concerns for any feed gas are reactant coal type (only anthracite used to date), $SO_2$ conversion percentage per reactor pass, COS, $H_2S$ formation, coal caking and gas distribution in the reactor. Preliminary economics of the Peabody absorption steam stripping and Bergbau Forschung systems combined with RESOX are presented in Table 1 and 2 along with dry sorption/baghouse collection/AI regeneration economics.

## Sodium Compound Reduction

The reduction of sodium compounds is a subsystem that can be combined with certain absorption schemes, regenerate sodium for reuse and produce elemental sulfur.

Sodium reduction can be accomplished by using the Tsukishima Kikai Engineering Company Process (TSK) which approximates a down-flow oil-fueled partial oxidation reactor with sodium solution introduced with the oil. Due to the temperature-time history of the solution in the reducer, sulfate compounds do not have sufficient time to react completely to carbonate but the sulfite usually can be converted(3). TSK technology, while it approximates Billirud Pulp and Paper industry technology, has not yet been commercialized for FGD and is not considered further in this paper.

Absorption schemes include the Rockwell International Aqueous Carbonate Process (ACP) developed by their Atomics International Division (AI)(4). This uses a unique spray dryer absorber and one of the prime candidates for the reducing subsystem - the AI molten salt reduction step (molten bath). The AI molten salt reduction step can reduce sulfite or sulfate due to the extreme

## TABLE 1
## PRELIMINARY ESTIMATED TOTAL CAPITAL REQUIREMENTS,[(a)]
## REGENERABLE FLUE GAS DESULFURIZATION PROCESS COMBINATIONS
500 MW at an Indiana Location and 1st Quarter of 1977

| Process | PEABODY/ FOSTER WHEELER RESOX[(b)] | FOSTER WHEELER RESOX[(b)] | DRY INJECTION[(c)] PLUS ATOMICS INTERNATIONAL REDUCTION[(b)] |
|---|---|---|---|
| Equipment and Material | 55.3 | 55.6 | 151.1 |
| Field Distributables | 8.4 | 17.2 | 21.0 |
| HQ Office | 8.4 | 2.9 | 17.8 |
| General Facilities and Owner Costs | 9.4 | 7.8 | 13.6 |
| Process Contingency | 7.1 | 2.0 | 9.6 |
| Project Contingency | 8.2 | 12.5 | 34.6 |
| Sales Tax | 1.3 | 1.5 | 3.8 |
| Total Plant Investment | 98.1 | 99.5 | 206.5 |
| Range | 93-113 | 95-114 | 194-244 |
| Reproduction Costs | 7.8 | 8.2 | 15.2 |
| Fees/Royalties | 5.5 | Included Above | 3.8 |
| Construction Loan Interest | 15.5 | 15.7 | 32.6 |
| Working Capital | 6.5 | 7.1 | 11.6 |
| Total Capital Requirement | 133.0 | 130.5 | 270.0 |
| Range | 127-152 | 124-150 | 254-317 |

Notes:
(a) All costs are $/kw
(b) Cost data subject to revision and re-estimate
(c) AI-ACP Process being estimated separately in follow-on work

## Table 2

## PRELIMINARY ESTIMATED ANNUAL TOTAL REVENUE REQUIREMENT FOR REGENERABLE FLUE GAS DESULFURIZATION PROCESSES
(1st QTR., 1977 Mills/kWh)

| | PEABODY/ FW RESOX[a] | BF/FW RESOX[a] | DRY INJECTION PLUS ATOMICS INTERNATIONAL REDUCTION[a] |
|---|---|---|---|
| Variable Costs | | | |
| Raw Materials | 1.04 | 2.64 | 0.98 |
| Utilities | 1.61 | 0.48 | 0.95 |
| Subtotal | 2.65 | 3.12 | 1.93 |
| Fixed Costs | | | |
| Maintenance | 0.59 | 0.99 | 1.53 |
| Operating Labor | 0.095 | 0.125 | 0.125 |
| Administrative and Support Labor | 0.10 | .148 | 0.22 |
| General and Administrative Expense | 0.20 | .296 | 0.44 |
| Property Taxes and Insurance | 0.406 | .405 | 0.87 |
| Other Expenses | 0.01 | - | - |
| Subtotal | 1.40 | 1.96 | 3.18 |
| Total Operating Cost | 4.05 | 5.1 | 5.1 |
| Cost of Capital | 3.25 | 3.2 | 6.6 |
| Total Revenue Requirement | 7.3 | 8.3 | 11.7 |
| Mills/kWh | 7.1-8.0 | 7.9-9.5 | 11.1-13.3 |

(a) All costs in Mills/kWh subject to revision and re-estimate processing technology steps used (more reference to the thermodynamics of sodium compound reduction will be given by Dr. P. S. Lowell in his paper given in this session (5)). The AI Aqueous Carbonate Process removes $SO_2$ and evaporates the solution in an innovative spray dryer contactor so it does not need extra energy for drying or for reheating, since it does not saturate the gas. The AI reduction step takes dry, crushed sodium salts (sulfite and sulfate) and feeds these pneumatically along with coal or coke into a refractory lined vessel. In this vessel a pool or bath of molten salt with a temperature around 1800°F reduces the sodium sulfate ($Na_2SO_4$) to sodium sulfide ($Na_2S$). The process then is somewhat similiar to Kraft paper pulping technology in that melt is quenched and dissolved (like green liquor in pulping). One major process difference is the use of coal with ash and the consequent ash contamination of the melt and solution. To remove ash, $SiO_2$ is precipitated out by lowering pH. The following filtration step is potentially difficult due to the gelatinous nature of the precipitate. Because of this filtration effect and the effect on the properties of the melt liquid and on tapping, ash contamination is a serious concern n the process. Ash contamination also makes application to dry sorption processes difficult since spent dry sorbents normally would be carrying the full burden of ash to the reducer. Testing of key process steps including coal ash effects will be carried on in an EPRI-Niagra Mohawk program at pilot scale. Follow-on efforts for an Empire State Electric Energy Research Corporation (ESEERCO) and EPA Joint demonstration program are underway.

The full range of processes that can be made by combining the reduction step with subsystems include conversion of simple sodium scrubbing or of sodium dual alkali scrubbing to sulfur production, regeneration of Wellman-Lord purge streams ($NaSO_4$) which are formed due to sulfite oxidation, and regeneration of spent dry sodium sorbent (such as nahcolite) which may be injected into the boiler back passes for $SO_2$ sorption. Simple sodium scrubbing and dual alkali scrubbing conversion implies spent sulfite/sulfate solution evaporation - either by ponds where possible or by heating. Obviously sodium solution evaporation by heating in order to feed the molten bath reduction step causes a severe heat rate penalty. This penalty is more than 500 Btu/kWh for a Midwest coal case using concentrated (20%) scrubbing solution. Simple sodium scrubbing in the West will be likely to produce high sulfate content salts due to the lower ratio of $SO_2$ to $O_2$ in the flue gas stream. Since oxygen transfer is relatively constant and since less sulfite is present due to lower $SO_2$, a higher percentage of sulfite is oxidized to sulfate. For this reason sodium/dual alkali and Wellman-Lord operation in the West may be more difficult. Both processes have difficulty in operating with sulfate. Dual alkali has problems reacting sodium sulfate to calcium sulfate and Wellman Lord must purge sulfate. The concept of adding a sulfate reducing loop to solve these problems is one option where disposal or sale of sodium sulfate is uneconomic or impractical.

A final combination with sodium reduction technology is the dry $SO_2$ removal or nahcolite injection FGD method. The advantages of this method in the throwaway mode are minimal equipment, no reheat requirements and a potential for reducing capital and operating costs. When using the AI Reducer technology the spent sorbent is dry and needs no evaporation. The problems for AI are ash contamination and required physical form of the regenerated reactant. Ash is intermixed and will cause melt character to change so the molten bath will not operate unless bulk removal of ash precedes the injection/$SO_2$ removal. The other problem is needing complex chemical and mechanical processing to regenerate bicarbonate (rather than carbonate in the ACP process) and to crystalize, dry, crush, size, convey and store the regenerated bicarbonate. EPRI has had Stone and Webster Engineering Corporation complete preliminary cost estimates for this combination (6). The cost of this combination is shown in Table 1 and 2. The ACP process is expected to be less expensive than the process described and is being estimated separately in follow-on economic study work done for EPRI by Stone and Webster Engineering Corporation.

## Aqueous Absorption/Steam Stripping

One system to symplify operations and potentially reduce cost is absorption/steam stripping (7). Dr. Gary Rochelle will address this topic in his paper later this session. The steam stripping concept is simple. An aqueous solution with suitable reagent absorbs the $SO_2$ and the solution is regenerated by indirect steam heating to evolve a concentrated $SO_2$ stream. The simplicity is an obvious advantage. The question is whether a suitable reagent can be found. Peabody Engineered Systems and Spring Chemical Corporation have both proposed new additives to be used in this process configuration. Peabody has proposed citric acid and Spring has proposed glyoxalic acid (Nobel Hoechst) as reagents. The theory of these approaches will be discussed by Dr. Rochelle. The advantages, if successfully developed, are simplicity and relatively low cost. The processes should be capable of being combined with $SO_2$ reduction to produce elemental sulfur or the product $SO_2$ fed to a sulfuric acid plant. The former case economics are illustrated in Tables 1 and 2. Additionally, where a market exists, $SO_2$ liquid can be sold directly. $SO_2$ liquid transport normally requires dried $SO_2$ and the stripper product does not normally meet this requirement.

The key process questions are steam use requirements for stripping, solution stability and operability on coal derived flue gases which have ash, chloride and trace element contaminants. EPRI intends to investigate this concept at least at lab scale to verify vendor claims and pursue this research line if claims are proven.

## Improve Existing Alkali Scrubbing Systems

Novel contactors may improve the performance , cost and reliability of current alkali scrubbing processes for FGD. For example, the problems of scaling and high pressure drop may be solved by simple designs such as the co-current contactor. This concept has been piloted at 0.7 MW scale (2200 ACFM) on coal derived flue gas at TVA's Colbert Station (8). This work was sponsored by EPRI. The concept uses a downflow co-current liquid spray-augmented flow with bulk liquid separation directly into the absorber sump via direction change. High gas velocities with resulting size and cost reduction, potential low droplet loadings to the mist eliminator and simple design are advantages. EPRI is sponsoring further work on a 10 MW scale with TVA at the Shawnee Test Facility.

The Chiyoda 121 process contactor will be described in a paper later this session. It could provide a single contactor that removes $SO_2$ with limestone and oxidizes the product to gypsum in one vessel. The reduction in unit operations and the elimination of recirculating slurry pumps may reduce costs and simplify maintenance. This design allows gypsum formation in a single step, without compromising the scale- preventing operating conditions common in calcium sulfite slurry scrubbing. This process is being considered by EPRI and the Southern Company for evaluation at Gulf Power's Scholz Station. Gypsum production should overcome the necessity for ponding. This has been demonstrated in the phosphate industry in Florida by their gypsum disposal practices (stacking).

### Clear Solution Scrubbing and Dual Alkali Improvements

The concepts of retrofitting lime and limestone scrubbing to utilize clear liquor scrubbing, to use limestone feed rather than to regenerate clear solutions (hence without lime calcining energy), and to produce gypsum rather than sludge are all useful or innovative concepts.

The DOWA's Basic Aluminum Sulfate/Gypsum process (9) can be used to retrofit lime/limestone scrubbers and meet these goals. This process uses acidic pH clear solution partially neutralized aluminum sulfate instead of lime or limestone slurry, and should not be susceptible to scaling. Calcium sulfate can be easily precipitated from the aluminum solutions and has the additional advantage of not leaching sodium compounds after disposal (as sodium dual alkali may do). Development of the DOWA process may be undertaken at 10 MW scale by EPRI and TVA in the latter part of 1978 at Shawnee Station.

The idea of modifying sodium lime dual-alkali to limestone regeneration is also receiving attention. CEA has done lab scale work to investigate this and further development is being contemplated by EPRI, EPA and Southern Company Services.

## Conclusions

Specific subsystems and processes show promise for reducing operating problems and cost, decreasing disposal impact and lowering energy use. Processes for reducing $SO_2$ to sulfur (Allied, Foster Wheeler) can be combined with concentrating processes (Wellman Lord and steam stripping). Sodium processes such as simple sodium scrubbing, dual alkali, and dry injection can be combined with sodium reduction techniques such as TSK and AI to reduce sodium use and disposal problems. Simple processes like steam stripping or Chiyoda 121 can be used to reduce operating complexity. New approaches that encourage limestone use and gypsum production will be emphasized. These approaches may increase availability and energy efficiency of the process feed and increase disposability of the product.

All of these concepts form a problem solving package for the utility industry. Many of the ideas are being actively evaluated by EPRI and utility company sponsors at the hardware stage. These evaluations will help utilities anticipate the costs and benefits of the concepts.

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# LIMESTONE/GYPSUM JET BUBBLING SCRUBBING SYSTEM

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## ABSTRACT

A development program initiated to integrate all the chemical and process steps of conventional limestone/gypsum processes into one vessel has led to the development of a new limestone based process employing a new, more efficient gas-liquid contacting device. Flue gas is sparged into the absorbent through an array of vertical spargers generating a froth for efficient gas-liquid contact. $SO_2$ is absorbed producing sulfite, which is oxidized to sulfate. Oxidizing air from the bottom supplies sufficient oxygen to completely oxidize the sulfite. Benefits derived from this new process are: simplicity of design, lower capital cost, energy conservation, elimination of slurry recycle and L/G in the traditional sense, essentially 100 percent calcium utilization, saleable or easily disposable gypsum byproduct, and elimination of calcium scaling problems.

An extensive research and development program that included operation of a 650-scfm pilot plant was conducted to provide prerequisite data and information for the design and operation of a prototype plant. Construction is now underway on a demonstration plant at Gulf Power Company's Scholz Steam Plant to demonstrate the cost and energy effectiveness and operability of this advanced technology.

# LIMESTONE/GYPSUM JET BUBBLING SCRUBBING SYSTEM

## INTRODUCTION

A research and development program was initiated by Chiyoda in 1975 to try and improve the reliability and cost to benefit ratio of direct limestone scrubbing systems by incorporating its commercially proven dilute acid scrubbing/gypsum technology.

From this concerted effort, it was found that reactions in the liquid phase, rather than the gas-liquid interfacial mass transfer, had a critical effect on the absorption of $SO_2$. It was also concluded that scrubbing $SO_2$ from the gas phase by contacting with water droplets as in spray and packed towers was less efficient than a process providing a continuous liquid phase with $SO_2$ removal effected by gas bubbling as in bubble cap columns. However, such conventional scrubber designs were not applicable to handling slurries. A new simplified design capable of achieving high mass transfer was needed.

Chiyoda's effort in this direction led to the development of a totally new gas-liquid contacting device, the basis of a new advanced process capable of high and efficient $SO_2$ and particulate removal. This device, called a Jet Bubbling Reactor (JBR), enabled Chiyoda to fully integrate and combine all the chemical and process steps of its dilute acid scrubbing/gypsum technology into one vessel, greatly reducing the complexities and inherent problems associated with lime/limestone scrubbing systems.

As a result, initial investment, energy consumption, and operating costs have been greatly reduced. Compared to conventional lime/limestone scrubbing systems, this new process features an improved and simplified plant design.

Although this new process, called the Chiyoda THOROUGHBRED 121, may be thought of as a variation of conventional lime/limestone scrubbing processes, there are distinct and advantageous differences, the most important of which are summarized below:

- Complete integration of all chemical and process steps
- Simplicity of plant design
- Elimination of slurry recycle loop (L/G in the traditional sense)
- Complete and controlled oxidation (Sulfite present in only trace amounts)
- Essentially 100% limestone utilization
- Saleable by-product with superior dewatering, handling and disposal characteristics
- Elimination of scaling problems
- Ease and stability of operation (No critical control parameters)
- Elimination of mist eliminator problems

## JET BUBBLING REACTOR

The operation and mechanism of the Jet Bubbling Reactor are depicted in the cut away view shown in Figure 1. The reactor is composed of two zones: a jet bubbling zone and a reaction zone.

Flue gas is sparged into a relatively shallow liquid layer through an array of vertical spargers having their open ends submerged 4 ∿ 16 inches below the liquid surface. A slotted gas sparger is schematically shown in Figure 2. High velocity gas (16 ∿ 66 ft/sec) entrains surrounding liquid creating a jet bubbling (froth) layer with a large gas-liquid interfacial area providing effective $SO_2$ removal. Sparging permits a gas superficial velocity on the order of several thousand $ft^3/ft^2$-hr, approximately ten times higher than the gas velocity in conventional bubbling columns and produces a froth characterized by high mass transfer. The gas contact time ranges from 0.5 ∿ 1.5 seconds.

The reaction zone is moderately stirred by both air bubbling and mechanical agitation. Oxidizing air is introduced at the bottom of this liquid zone at several times the stoichiometric requirement. The liquid residence time, 1 ∿ 4 hours, is conducive to such slow steps as limestone dissolution and gypsum crystal growth.

The liquid flow pattern of the two zones is shown in Figure 3. As can be seen, the liquid circulation continuously supplies regenerated absorbent to the jet bubbling layer, eliminating the need for an external slurry circulation loop (characteristic of conventional wet scrubbing process) resulting in energy conservation.

The JBR is a single vessel, consisting of flue gas inlet and outlet, air inlet, limestone slurry inlet, and gypsum slurry outlet. Air and mechanical agitation are also provided. The $SO_2$ in the flue gas is absorbed, oxidized and neutralized in this single reactor.

## PROCESS CHEMISTRY

The chemistry of this new process is similar to that of conventional limestone scrubbing processes, but definitely different in that $SO_2$ is completely and intentionally oxidized to sulfate (gypsum), leaving only trace amounts of sulfite. Additionally, all chemical and process steps are carried out in one vessel.

Overall reaction equation for the system:

$$SO_2 + CaCO_3 + \frac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

As illustrated in Figure 1, the Jet Bubbling Reactor can be divided into two zones which are both liquid phase continuous.

Reaction equations in the jet bubbling (froth) zone:

$$SO_2(g) \rightleftarrows SO_2(aq)$$
$$SO_2(aq) + H_2O \rightarrow H_2SO_3$$
$$H_2SO_3 \rightleftarrows HSO_3^- + H^+$$

$$HSO_3^- \rightleftharpoons SO_3^{--} + H^+$$
$$SO_3^{--} + \tfrac{1}{2}O_2(aq) \rightarrow SO_4^{--}$$
$$CaCO_3(s) \rightleftharpoons CaCO_3(aq)$$
$$CaCO_3(aq) + H^+ \rightleftharpoons Ca^{++} + HCO_3^-$$
$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$
$$Ca^{++} + SO_4^{--} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

Reaction equations in the reaction (liquid) zone:

$$O_2(g) \rightleftharpoons O_2(aq)$$
$$SO_3^{--} + \tfrac{1}{2}O_2(aq) \rightarrow SO_4^{--}$$
$$CaCO_3(s) \rightleftharpoons CaCO_3(aq)$$
$$CaCO_3(aq) + H^+ \rightleftharpoons Ca^{++} + HCO_3^-$$
$$Ca^{++} + SO_4^{--} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$$
$$CaSO_4 \cdot 2H_2O \rightarrow \text{growth}$$

For the jet bubbling zone, gas phase mass transfer of $SO_2$, dissolution of $CaCO_3$ and hydration of $SO_2$ to give $H^+$ are the controlling steps. For the reaction zone, liquid phase mass transfer of $O_2$ and gypsum crystal growth are the controlling steps.

## PROCESS DESCRIPTION

A schematic process flow diagram is given in Figure 4. The flue gas is introduced directly into the Jet Bubbling Reactor, quenched with water, and then sparged into the absorbent through an array of vertical spargers, generating a jet bubbling (froth) layer. $SO_2$ is absorbed in the jet bubbling layer producing sulfite which is oxidized completely to sulfate. The cleaned flue gas then flows out the reactor through a mist eliminator and out the stack.

Limestone slurry is pumped directly to the Jet Bubbling Reactor to precipitate sulfates as gypsum. The crystallized gypsum by-produced, discharged from the reactor at a slurry concentration of 10 ∿ 25 wt.%, is pumped to the gypsum stack. The solids settle out by gravity and the supernatant (stack overflow) pumped back to the process.

A mixture of gas, liquid, and solids in the reactor is maintained by gas bubbling and mechanical agitation.

Gypsum By-product: The gypsum by-product is of high purity, typically 95 wt.% and higher depending on the quality of the limestone used. Its average crystal size is 50 ∿ 100 microns in Stokes' diameter and its settling velocity is greater than 10 ft/hr. The gypsum by-product is easily dewatered, typically to 85 ∿ 95 wt.% solids using centrifugation equipment or 80 ∿ 90 wt.% using filtration equipment. Filtration rates of up to 4,500 lbs/hr per square foot are expected. It can also be thickened to a solids concentration of 70 wt.% by gravity.

Gypsum, the dihydrate form of calcium sulfate, is one of the most stable sulfur compounds known. It is harmless to man and has been widely used since the Egyptian Pharaohs first used it as mortar in the construction of pyramids. Today gypsum is used primarily in the manufacture of wallboard, portland cement, and in agriculture as fertilizer and soil conditioner.

## DEVELOPMENT AND PILOT PLANT OPERATION

An extensive research and development program that included operation of a 650 scfm pilot plant was conducted to provide prerequisite data and information for the design and operation of a prototype plant.

A schematic process flow diagram of the pilot plant is shown in Figure 5. The pilot plant is a fully integrated system incorporating all the features of a prototype design. Major equipment items together with their sizes and materials are listed in Table 1.

### Pilot Plant Test Results

The pilot plant has been in operation since 1975, and has been operated at both high and low sulfur conditions. Flue gases are generated by burning high or low sulfur heavy fuel oil.

The major items tested were:

- $SO_2$ removal
- Particulate removal
- Limestone utilization
- Operability
- Scaling
- Gypsum by-product
- Sparger design

Typical pilot plant operating conditions and test results are given in Table 2. Physical properties of the by-product gypsum are presented in Table 3.

These test results show high $SO_2$ removal capability, essentially 100% limestone utilization, and a sulfite-free, high purity gypsum by-product.

Limestone Utilization: The pH or acid concentration value was found to be the most important variable affecting limestone utilization. From Figures 6 and 7, it can be seen that limestone utilization decreases with increasing pH and that limestone utilization is nearly 100% at a pH of less than 4.5. It is of significance that even for an extended residence time of four hours, high pH operation did not give satisfactory limestone utilization.

Scaling: Sulfate scaling problems are generally known to be associated with dissolution and precipitation of solids. By maintaining a gypsum crystal concentration within the range of 10 $\sim$ 20 wt.%, and having sufficient liquid volume, the area for gypsum crystal growth is increased and the degree of supersaturation decreased. As a result, gypsum precipitates only on the surfaces of gypsum crystals eliminating calcium sulfate deposition or scaling on the reactor walls and internals.

Calcium carbonate and calcium sulfite scaling problems were not a problem due to complete oxidation of sulfite, nearly 100% calcium utilization and optimally selected pH and reaction capacity per volume.

*Mist Eliminator:* Mist eliminator problems were not encountered during pilot plant operation due to complete oxidation of sulfite, high limestone utilization and low entrainment.

*Particulate Removal:* High particulate removal capability of the jet bubbling (froth) layer was confirmed during a series of particulate removal tests with the prescrubber bypassed. Removal efficiencies of 90% were achieved.

*Fluid Dynamics:* In addition to the integrated pilot plant testing, a separate facility was constructed with lucite panels (for visual observation of flow pattern and stability) and operated to study gas-liquid flow dynamics. A series of tests was conducted with air flows ranging from 650 ∿ 12,000 scfm. From these studies the optimum gas sparger design was developed.

## ECONOMICS

On the basis of the pilot plant test, process economics were developed. Table 4 lists the capital and annualized operating costs based on a 200 MW coal-fired boiler burning 3% sulfur coal, 70% load factor, 90% $SO_2$ removal requirement, and ponding or stacking of the gypsum by-product. The process flow is the same as that discussed earlier in the PROCESS DESCRIPTION section, and shown in Figure 4.

## FEATURES AND ADVANTAGES

The pilot plant tests have shown that capital and operating cost and energy consumption can be greatly reduced and excellent desulfurization and operability achieved by combining all the process and chemical steps into one vessel. The salient feature of the CT-121 process is the innovative and compact Jet Bubbling Reactor which combines the absorption, oxidation, neutralization and crystallization processes all into one vessel. The advantages derived from this feature are summarized below:

- Simplified Plant Design

  As a result of single vessel simplicity, significant reductions in process equipment, piping, and plot area are achieved.

- Low Investment and Low Operating Costs

  The smaller number of process equipment, required plot area, and highly efficient utilization of energy and alkali result in low initial investment and operating costs.

- Elimination of Slurry Recycle Loop

  L/G (in the traditional sense) has been eliminated. Absorbent is supplied by air and mechanical agitation, resulting in energy conservation.

- Easy and Stable Operation

  The only required process control parameter is the adjustment of the limestone feed rate. There are no critical control parameters. A wide range of boiler fluctuations can be tolerated without deleterious effect.

- No Scaling Problems

  Although slurry is used for the absorbent, it contains sufficient gypsum seed crystals to prevent the deposition of the reaction products on the surfaces of the reactor walls and internals.

- Essentially 100% Limestone Utilization

  By maintaining the pH at a relatively low value, complete and controlled oxidation is achieved enhancing gypsum formation and alleviating scaling problems.

### Gypsum By-product

There is essentially no limestone or sulfite in the gypsum by-product. The useful and saleable by-product is of high purity and can be marketed to wallboard and portland cement manufacturing plants or sold without further treatment or processing as fertilizer. In addition, disposal cost of Chiyoda gypsum are substantially less. Its physical properties and superior dewatering and handling characteristics allow it to be stacked, minimizing land requirement and ponding costs.

## DEMONSTRATION OF 20-MW PROTOTYPE PLANT

Construction is now underway on a 20-MW prototype demonstration plant at Gulf Power Company's Scholz Steam Plant, Sneads, Florida, to corroborate and demonstrate the performance, reliability, operability and the cost and energy effectiveness of this advanced technology. The test unit is expected to be operational in June 1978.

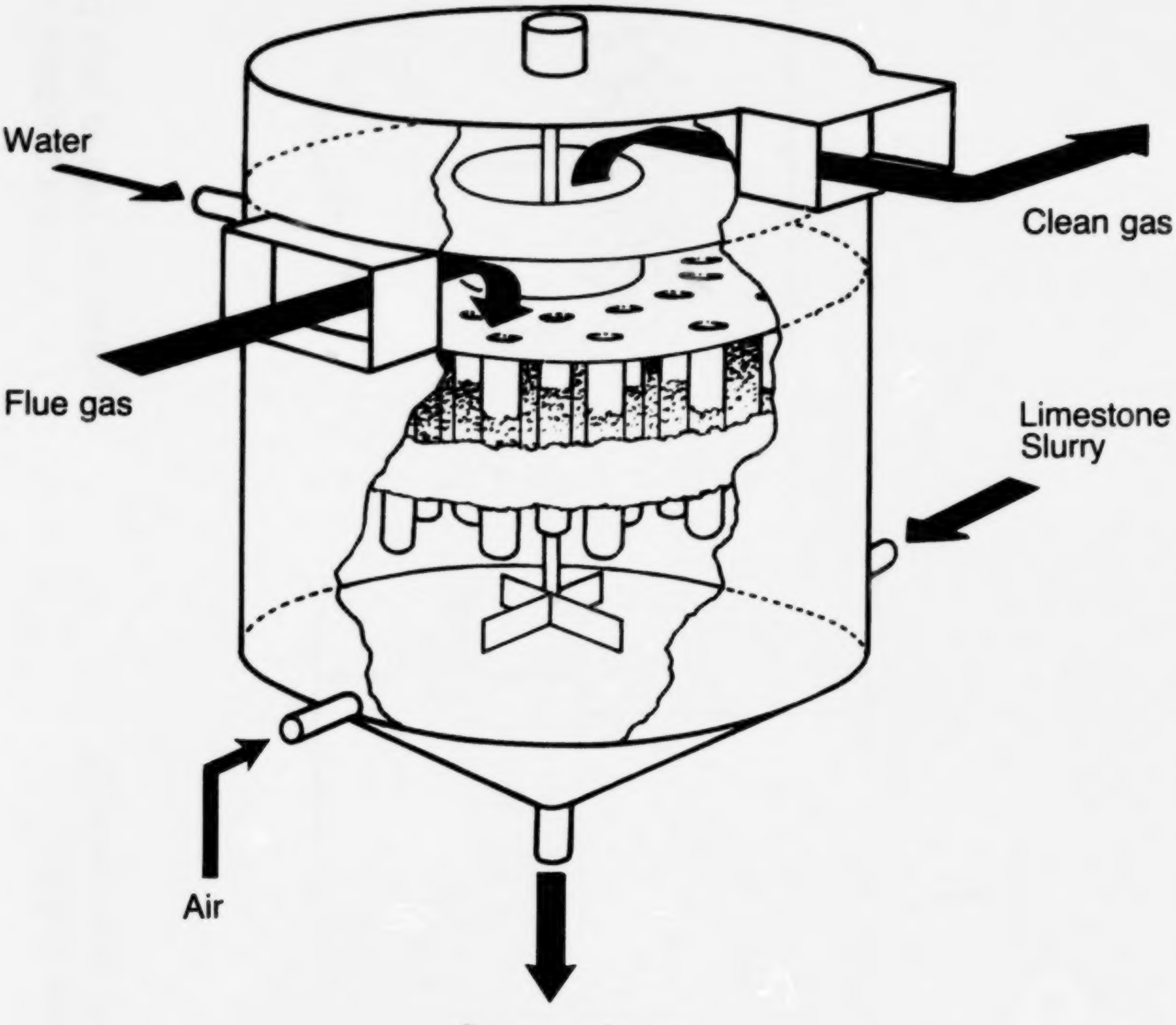

Figure I. Jet Bubbling Reactor.

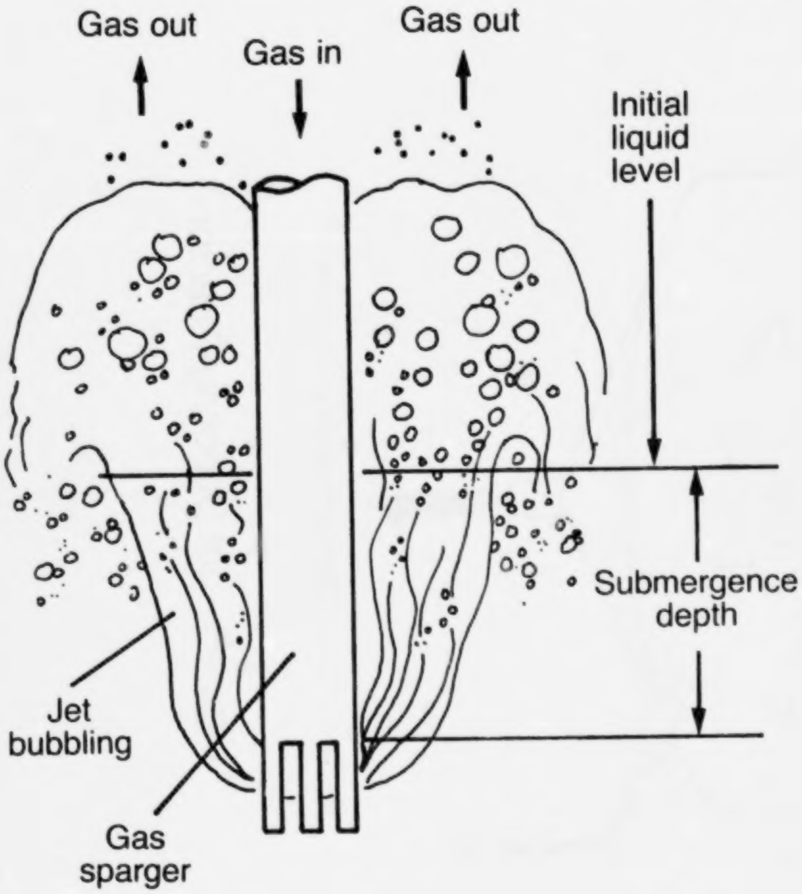

Figure 2. Schematic drawing of gas sparger.

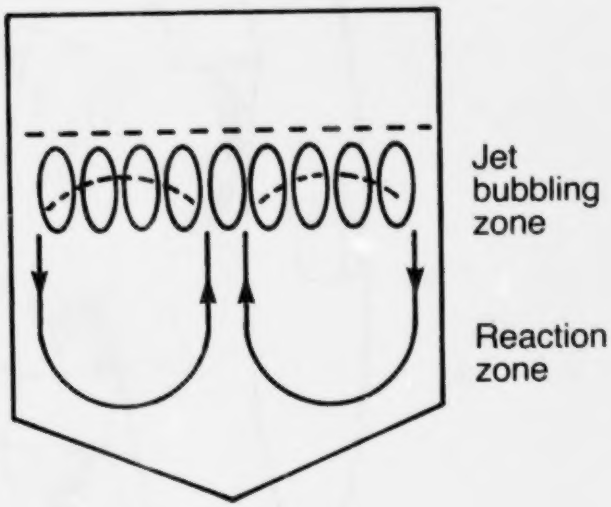

Figure 3. Liquid flow pattern in jet bubbling reactor.

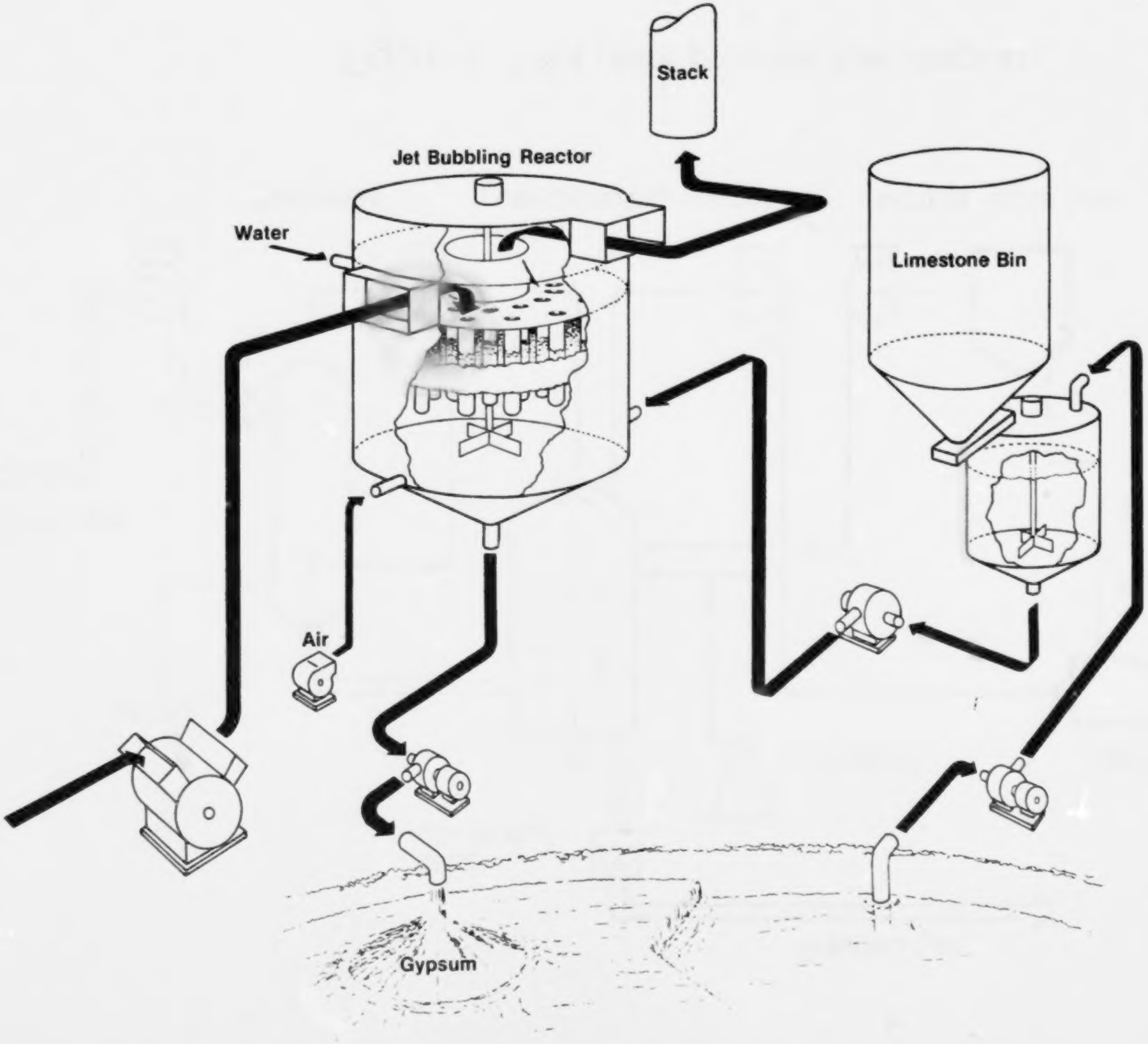

Figure 4. Process flow diagram of prototype plant.

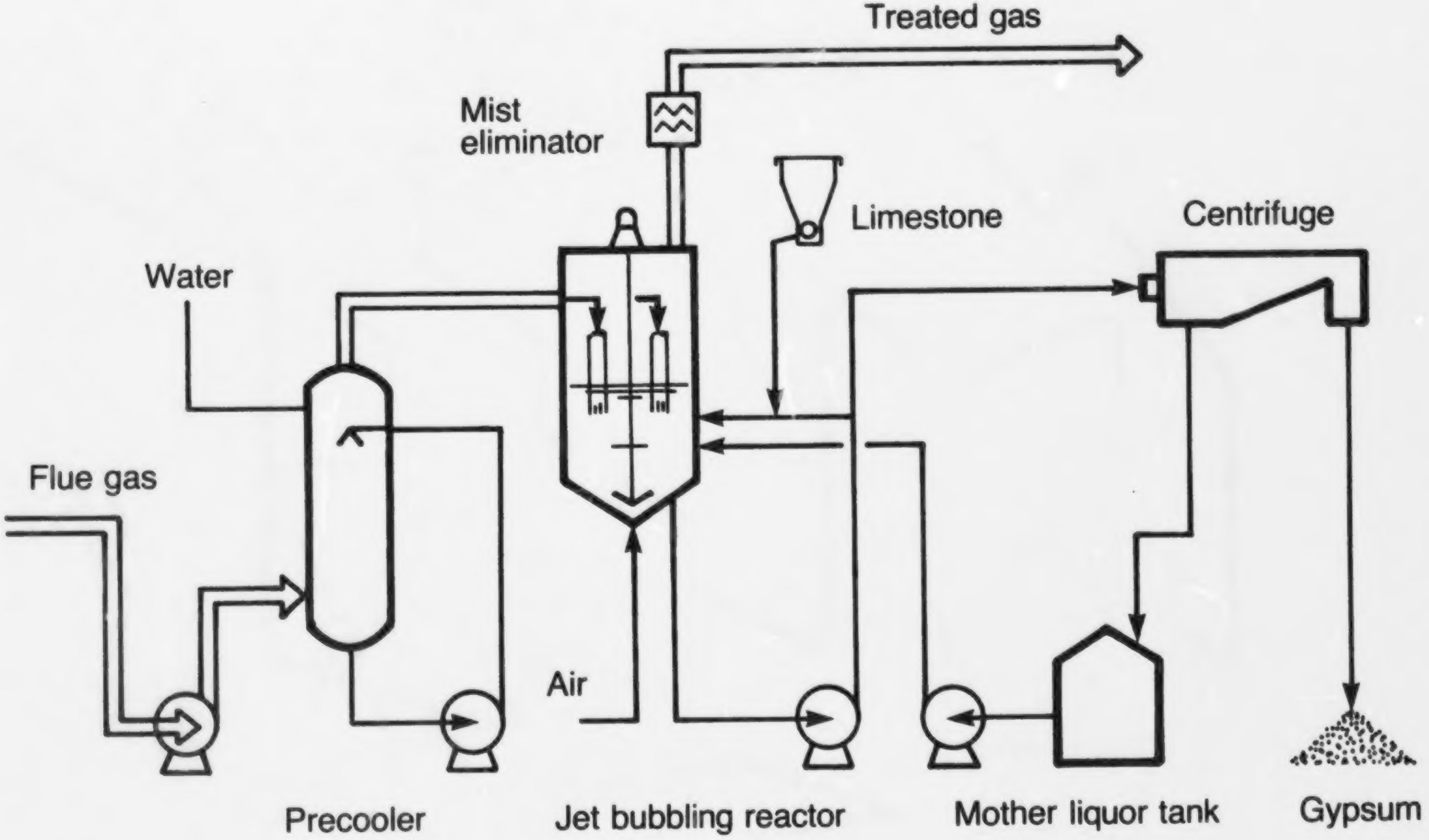

Figure 5. Pilot plant process flow diagram.

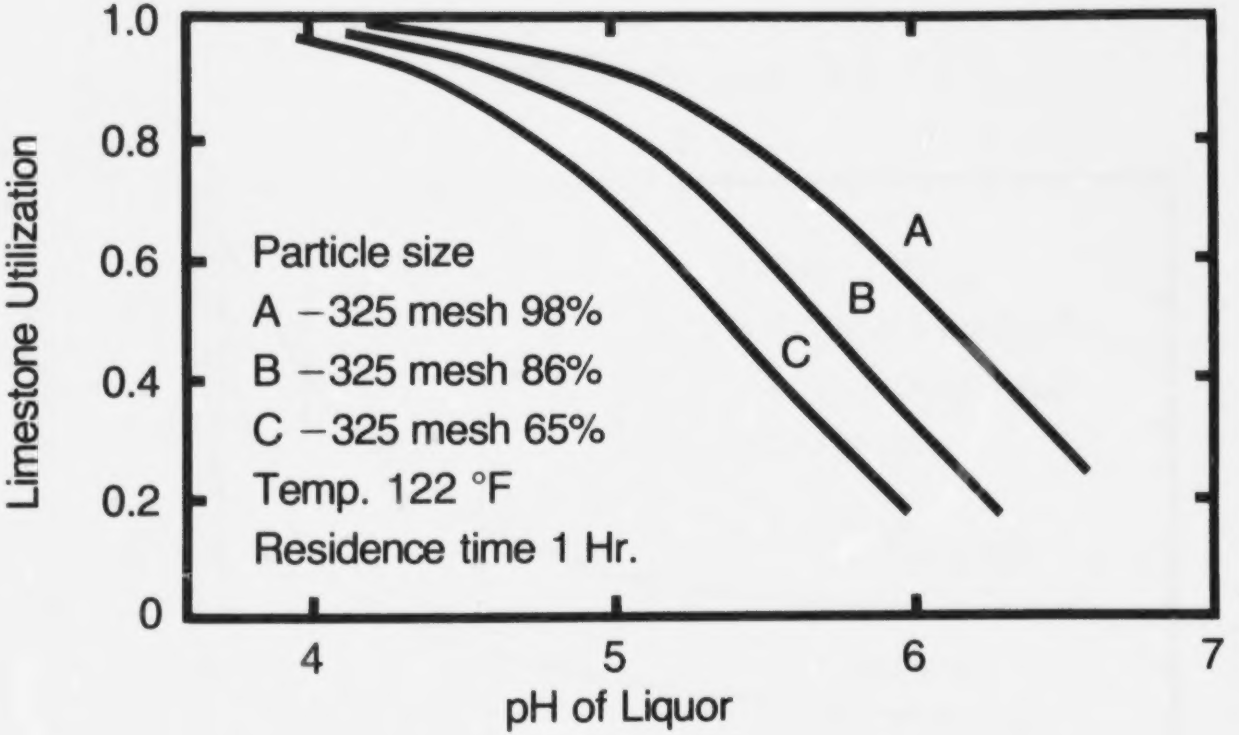

Figure 6. Effect of pH on limestone utilization.

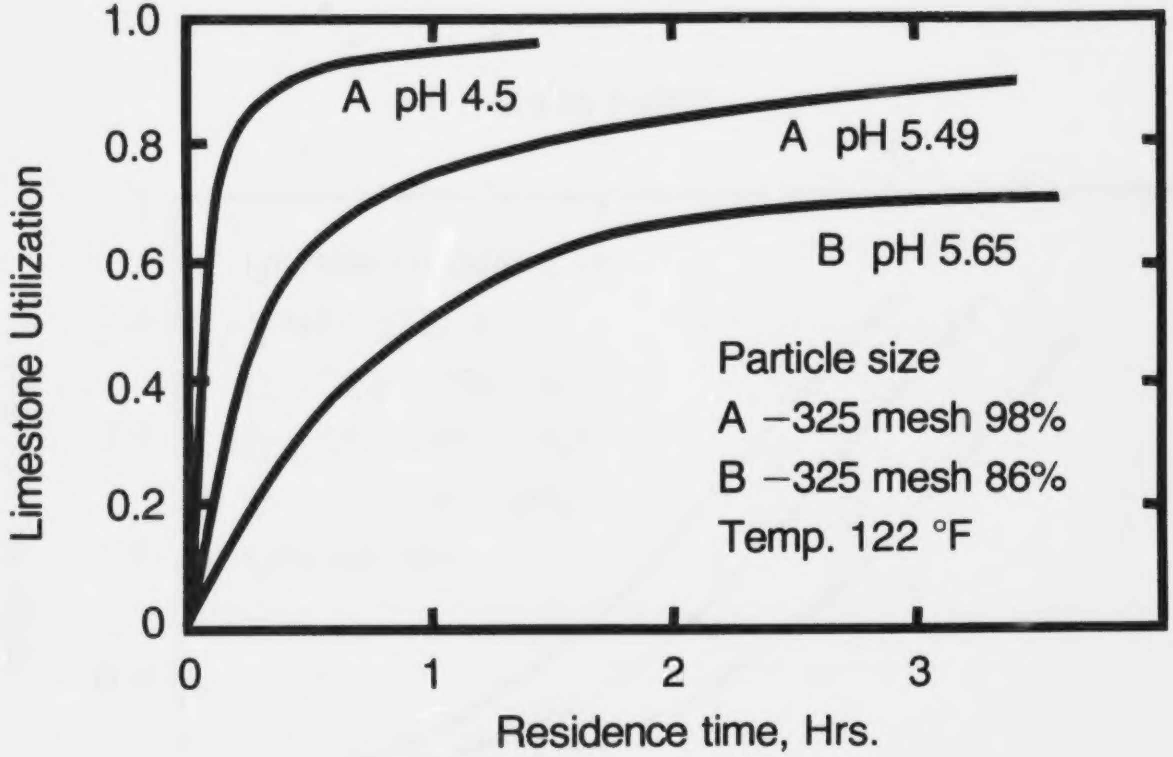

Figure 7. Effect of residence time on limestone utilization.

## Table 1. MAJOR EQUIPMENT OF PILOT PLANT.

| Equipment | Type | Size | Material |
|---|---|---|---|
| Precooler | Spray Column | 2.3' dia. × 10.5' ht. | 316L S.S. |
| Jet Bubbling Reactor | | 1.6' dia. × 13.1' ht. | " |
| Mother Liquor Tank | | 4.9' dia. × 8.5' ht. | FRP |
| Flue Gas Blower | Turbo | 650 SCFM @ 27.5"$H_2O$ | C.S. |
| Cooling Water Circulation Pump | Centrifugal | 4.4 gpm @ 65.6' $H_2O$ | Rubber Lining |
| Gypsum Slurry Pump | " | 22.0 gpm @ 65.6' $H_2O$ | " |
| Mother Liquor Pump | " | 13.2 gpm @ 65.6' $H_2O$ | " |
| Centrifuge | Screw Decanter | | Stellite + 316L S.S. |

## Table 2. TYPICAL PILOT PLANT OPERATING DATA.

| Conditions | | Typical Values | |
|---|---|---|---|
| | | Low Sulfur Case | High Sulfur Case |
| Flue Gas Flowrate to Precooler | SCFM on wet basis | 585 | 585 |
| Flue Gas Temperature | °F | 135 - 140 | 135 - 140 |
| Flue Gas Composition | | | |
| $SO_2$ | ppm on wet basis | 1,000 - 1,100 | 2,900 - 3,000 |
| $O_2$ | % on wet basis | 2.9 - 3.2 | 2.9 - 3.2 |
| $CO_2$ | " | 11.0 - 11.5 | 11.0 - 11.5 |
| $H_2O$ | " | 16.5 - 19.0 | 16.5 - 19.0 |
| $SO_2$ Loading @JBR Outlet | ppm on wet basis | 77 - 85 | 360 - 380 |
| $SO_2$ Removal | % | 92 | 87 |
| Temperature of JBR Liquid | °F | 135 - 140 | 135 - 140 |
| Oxidation Air | SCFM | 12.4 | 31.0 |
| Pressure Drop of JBR | in. H2O | 13.8 - 15.8 | 13.8 - 15.8 |
| Limestone Utilization | % | 99.3 | 99.1 |

## Table 3. GYPSUM QUALITY.

| | |
|---|---|
| Particle Size: | |
| Average Stokes' diameter | 60 micron |
| Chemical Composition (wt %): | |
| CaO | 32.14 |
| $SO_3$ (Sulfate) | 45.59 |
| as $CaSO_4 \cdot 2H_2O$ | 98.02 |
| $CaSO_3$ (Sulfite) | undetectable |
| $CO_2$ | 0.18 |
| as $CaCO_3$ | 0.41 |
| ph | 6.8 |
| Free Water (wt % on wet basis) | 13.5 |
| Mortar Strength (psi): | |
| Tensile | 135 |
| Compression | 640 |
| Bending | 384 |

## Table 4. CAPITAL AND OPERATING COSTS FOR 200 MW UNIT.

Design basis: 70% load factor, 3% sulfur coal, 90% $SO_2$ removal efficiency.

| Item | | Unit | Jet Bubbling FGD |
|---|---|---|---|
| Capital Cost | | $ | 6,200,000 |
| Annual Operating Cost: | | | |
| Electricity | $ 0.02 / KWH | $/Year | 418,200 |
| Process water | $ 0.1 / 1000 gal. | " | 8,700 |
| Cooling water | $ 0.05 / 1000 gal. | " | 7,000 |
| Limestone | $ 10 / ton | " | 360,000 |
| Labor | $ 7.85 / man-hour | " | 120,000 |
| Maintenance | 3% of Capital Cost | " | 186,000 |
| Sub Total | | | 1,099,900 |
| Capital Charge | 17.5% of Capital Cost | " | 1,085,000 |
| Overhead | 10% of Direct Cost | " | 109,990 |
| Total | | " | 2,294,890 |
| Capital Cost per KW | | $/KW | 31.00 |
| Annuallized Cost | | mills/KWH | 1.87 |

# OPTIONS FOR $SO_2$ REDUCTION

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## ABSTRACT

Several of the more promising recovery-type FGD processes produce a concentrated stream of $SO_2$ that must then be converted to sulfuric acid or sulfur, preferably the latter. This paper analyzes the various processes that can be used for reducing the $SO_2$, with emphasis on use of coal as the reducing agent. Experience in using coal for direct reaction with $SO_2$ is reviewed, as well as gasification of coal or heavy oil to give $H_2$, CO, or syn gas as the reductant and to give an $H_2S/SO_2$ mixture suitable for the Claus reaction. Finally, both dry and wet Claus processes are discussed, particularly in regard to integration into an overall FGD system. Costs are given wherever meaningful data could be obtained and the comparative economics of sulfur as an FGD product are analyzed.

# OPTIONS FOR $SO_2$ REDUCTION

## Introduction

Most of the power plant FGD systems in current operation are of the "throwaway" type, producing an end product sludge or mixture of sulfur compounds which must be disposed of as a waste product. Extensive developmental work is underway on regenerable FGD systems that will produce either sulfuric acid or elemental sulfur as the end product. Many of the regenerable FGD processes produce an intermediate $SO_2$-rich product gas. For example:

| | %v $SO_2$ | %v $H_2O$ | %v $N_2$, $O_2$, $CO_2$ |
|---|---|---|---|
| Wellman-Lord | 85-90 | 10-15 | -- |
| Shell-UOP CuO | 85-90 | 10-15 | -- |
| Citrate (with stripping) | 90 | 10 | -- |
| TVA ammonia-ABS | 65 | 1-2 | 33-34 |
| Bergbau-Forschung | 20 | 60 | 20 |
| Magnesia slurry | 8-10 | 10 | 70-80 |

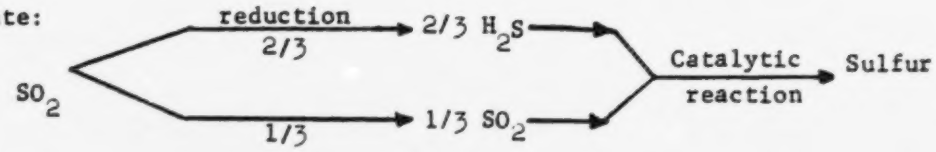
The purpose of this paper is to discuss some of the process options by which the $SO_2$-rich gas from a regenerable FGD system can be converted to elemental sulfur. For many electrical utility companies, elemental sulfur would be the preferred end product because:

- Sulfur is easily handled, stored and shipped (either in dry or molten form).
- Sulfur can be sold for use in many industrial applications.

In general, the production of sulfur from $SO_2$ requires the chemical reduction of $SO_2$ either directly to elemental sulfur or through the intermediate reduction of some of the $SO_2$ to $H_2S$:

Direct: $SO_2 \xrightarrow{\text{reduction}} \text{Sulfur}$

Intermediate:



An example of the direct reduction using carbon as the reductant would be:

$$C + SO_2 \longrightarrow CO_2 + S$$

which is the basic chemistry underlying the RESOX process for converting $SO_2$ to sulfur.

An example of the intermediate reduction of $SO_2$ using either hydrogen or carbon monoxide as the reductant would be:

$$SO_2 + 3H_2 \longrightarrow H_2S + 2H_2O$$

$$SO_2 + 3CO + H_2O \longrightarrow H_2S + 3CO_2$$

By combining the $H_2S$ with the remaining $SO_2$, elemental sulfur is produced via the classical Claus reaction:

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

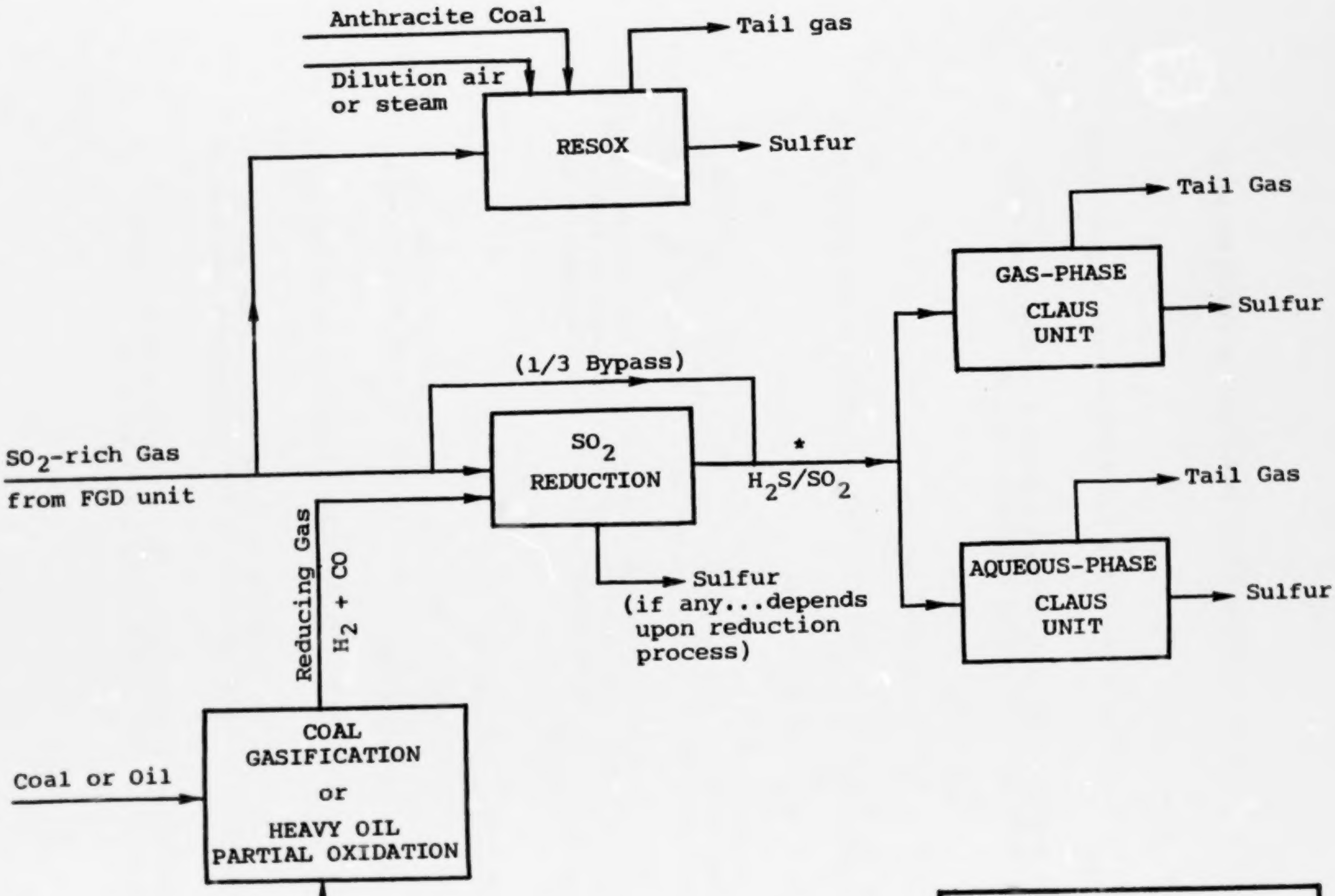
Thus 3 mols of reductant ($H_2$ + CO) is required to reduce 1 mol of $SO_2$ to the intermediate $H_2S$. However, the overall conversion of $SO_2$ to sulfur via the intermediate method only requires 2 mols of reductant ($H_2$ + CO).

Methane could also be used as a reductant but the current energy shortage involving natural gas (methane) and petroleum makes it highly unlikely that methane can be seriously considered as a reductant for use in power plant FGD systems.

## Process Routes From $SO_2$ to Sulfur

Figure 1 is a schematic flow sheet of the process routes for converting FGD-derived $SO_2$ to sulfur as they will be considered in this paper. It depicts the following:

- The direct reduction of $SO_2$ to sulfur using coal carbon via the RESOX process.
- The conversion of $SO_2$ to sulfur in Claus units (either gas or liquid-phase) using $H_2S$ produced by the intermediate reduction of $SO_2$.
- The production of reducing gas ($H_2$ + CO) from either coal gasification or the partial oxidation of heavy oil.



* 2/3 of $SO_2$ reduced to provide Claus feed gas of 1/3 $SO_2$ and 2/3 $H_2S$ by volume

OPTIONS FOR PRODUCING SULFUR FROM FGD $SO_2$

FIGURE 1

Another process option which could be considered, and which is not included in this paper for the sake of brevity, is the intermediate production of $H_2S$ by the reduction of a portion of the end product sulfur.

## Direct Reduction by the RESOX Process

Although the simplest approach is direct reduction with bituminous coal, the impurities in coal make this a difficult route. The earliest effort on direct reduction seems to have been the work by Consolidated Mining and Smelting (now Cominco) in British Columbia, in which a concentrated $SO_2$ stream obtained by thermal stripping of ammonia scrubber effluent solution was passed through a bed of hot coke along with oxygen. The method was reasonably successful but was abandoned in favor of an acidification process that produced sulfuric acid and ammonium sulfate.

More recently, the Foster Wheeler Energy Corporation has done pilot plant work on a similar process using anthracite coal instead of coke; the method is called RESOX (Fig. 2; Bischoff, 1975). The pilot-plant work is reported to have been promising (Steiner, 1974) but tests at Gulf Power's Scholz station in a 20-mw experimental unit were not conclusive. Currently, EPRI is developing a program with the federal government of West Germany in which RESOX will be tested in conjunction with the 45-mw carbon adsorption unit now being operated at STEAG's Kellermann station in Lunen. The carbon system (Bergbau-Forschung) produces a fairly rich stream of $SO_2$ (about 20%) suitable for feed to the RESOX unit.

One of the main features of the RESOX process is use of steam along with the $SO_2$ in order to make operation practicable at relatively low temperature, in the range of 1100 to 1500° F as compared to 2200 to 2300° F in the Cominco tests--in which use of steam was not emphasized. The effect of $H_2O/SO_2$ ratio in the pilot plant tests is shown in Fig. 3.

One of the problems is that elemental sulfur is not the only product; $H_2S$, COS, $CS_2$, and other sulfur compounds are formed in significant amounts depending on various factors. For example, Fig. 3 shows that about 4 mols of $H_2O$ are required per mol of $SO_2$ to get an $SO_2$ reduction of 90% or higher. However, the high $H_2O/SO_2$ ratio also promotes formation of $H_2S$ rather than S when the temperature is above 1200° F. Sulfur formation is favored at lower temperature but conversion falls off as temperature is decreased. Under conditions that give 100% $SO_2$ reduction, the product is about 90% sulfur and the remainder other sulfur compounds.

There are several other questions that need to be resolved in further work on the process.

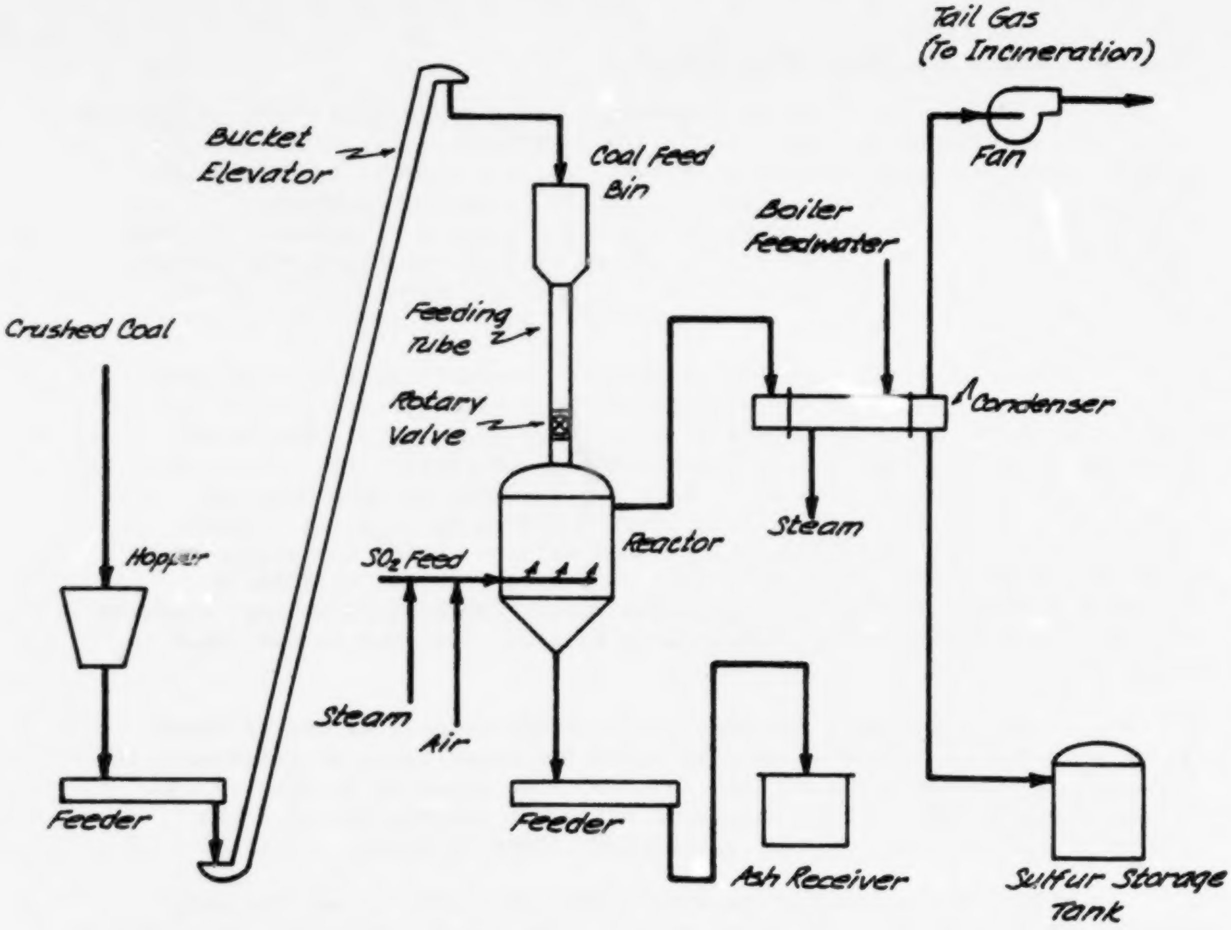


FIGURE 2
RESOX PROCESS

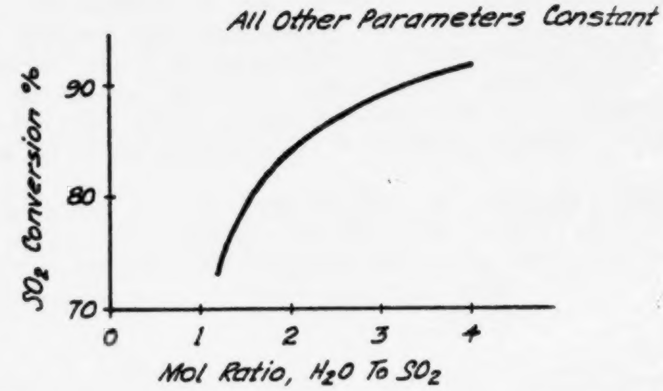


FIGURE 3
EFFECT OF WATER VAPOR IN RESOX PROCESS

1. Adaptability to various front-end systems. RESOX requires a low oxygen content in the feed gas in order to prevent carbon combustion. Wellman-Lord and Bergbau-Forschung off-gas seem acceptable but not that from magnesia scrubbing. The Bergbau gas is quite suitable since it already has the proper $H_2O/SO_2$ ratio (see earlier), but $H_2O$ can be added in other processes.

   Low $SO_2$ in the feed gas would also reduce degree of reduction. At 25% $SO_2$, about 90% conversion to sulfur would be expected but at 5% $SO_2$ only 75%. Below 3% $SO_2$ the efficiency falls off drastically.

2. Use of bituminous coal. Although use of anthracite is probably acceptable from the economic standpoint, the process would be much improved if bituminous coal could be used. There is some indication that this can be done, with the volatiles acting also as reductants. The main problem is in using caking-type coals, for which a precarbonization step probably would be necessary.

3. Temperature control. Because of the several variables, reactor temperature is best controlled by adjusting conditions to give a temperature somewhat below optimum and then adding air for "trimming". This makes any variation in the oxygen content of the inlet gas a problem.

4. Energy efficiency. The coal is only about half consumed in the reduction step. It is proposed to use the residue either as fuel in the boiler or as an adsorbent for $SO_2$ (in the Bergbau-Forschung process). Each of these presents some problems.

5. Sulfur condensation and purification. The dust and other impurities in the sulfur vapor evolved from the reduction vessel cause problems in condensation and purification.

Notwithstanding these difficulties, direct reduction with coal is a relatively simple and promising approach.

Capital cost estimated for RESOX in 1975 was $6.50 per kw for a 500-mw boiler burning 4.3% S coal (Bischoff and Steiner, 1975). This is a preliminary estimate, however, and subject to change as more is learned about the process in the STEAG tests. More recent estimates are in the range of $8 to $16 per kw.

For coal gasification, Table 3 (see later) indicates a capital cost of $8 to $10 (1000 mw) for the gasifier alone, with the Claus unit still to be added for getting to elemental sulfur. The latter adds $5 to $6 giving a total of $13 to $16 per kw. Scaling this to 500 mw gives $20 to $25 as compared to the $8-16 estimated for RESOX. Thus RESOX is likely to retain a considerable capital cost advantage even if the development work indicates a higher cost than now estimated.

For annualized cost, Table 3 shows that capital charges and cost of coal make up over 90% of the total cost of gasification, with the two about even at $30 per ton of coal. The amounts of coal for RESOX and gasification-Claus appear to be roughly the same but if anthracite is required for RESOX the coal expense items will be larger because of the higher cost of anthracite. Thus the capital charges for RESOX are likely to be less than for the gasification route but the coal cost may be higher. A definitive comparison cannot be made at this time; much depends on whether RESOX can be adapted to bituminous coal and what the capital cost turns out to be.

## Coal Gasification to Produce Reducing Gas

Coal gasifiers that operate at essentially atmospheric pressure are best suited for the application considered in this paper since hydrogen and carbon monoxide are the desired products (rather than methane) and since the product reducing gas is only required at a low pressure. The commercially available atmospheric pressure gasifiers include (McCaleb, 1977; Bodle, 1974; Farnsworth, 1973, 1974; Banchik, 1973, 1975):

- Koppers-Totzek
- Winkler
- Wellman
- Riley-Morgan
- Wilputte

The low pressure gasification of coal has a long history of commercial usage, primarily for the production of "town gas" and chemical synthesis gas. For example, Koppers-Totzek can point to 48 gasifiers in 16 world-wide locations, and Winkler to 36 gasifiers in 16 locations. Other than updating the designs to accommodate current environmental restrictions on air pollution, wastewater, and waste solids disposal, coal gasification can be considered to be commercially proven technology.

Table 1 is a comparison of the available atmospheric pressure gasifiers; some of the key points are:

- Koppers-Totzek is primarily limited to the use of oxygen blowing.
- Winkler and Wellman can be designed for either air or oxygen.
- Riley-Morgan and Wilputte are primarily limited to air blowing.
- Those gasifiers operating at above 1200° F (Koppers-Totzek and Winkler) produce no tars, oils or phenols. The others operate below 1200° F and will produce such impurities.

From the viewpoint of capital cost and of operational simplicity, the need to provide oxygen for gasification is probably a drawback for the application considered in this paper. From the viewpoint of wastewater treatment requirements as well as operational simplicity, a gasifier which does not produce tars, oils or phenols would be preferable. Hence, on a purely qualitative basis, the Winkler gasifier is probably the best "fit" for providing reducing gas to FGD systems. However, a quantitative economic analysis of the alternative gasifiers should be made before making a selection in any specific case.

Table 2 defines the $SO_2$ reduction needs for a 1000 mw power plant FGD system, based upon burning 3.5 wt % sulfur coal and removing and recovering 90% of the coal sulfur in a regenerable FGD unit. The total $SO_2$ recovered by the FGD unit would be 630 tons/day and 2/3 of that, or 420 tons/day, would need reduction to $H_2S$ for use in the subsequent Claus plant to produce elemental sulfur. The amount of ($H_2$ + CO) reductant required would be 14.9 MM SCF/day.

As shown in Table 2, based upon the reductant ($H_2$ + CO) yields in Table 1, the amount of dry coal that would need to be gasified ranges from 250-300 tons/day. Depending upon which gasifier type is selected, the number of commercially available modules would range from 1 to 5 excluding any modules needed to provide the desired onstream reliability.

Table 3 presents the estimated capital investment and annualized costs of an air-blown gasification plant for producing 14.9 MM SCF per day of reductant ($H_2$ + CO) from 300 tons/day of coal:

- Capital investment = $8,000,000-$10,000,000
- Annualized costs = 0.58-0.77 mills/KWH of power plant output (assuming a 75% load factor)

Battelle has also estimated gasification costs, in a study for EPA (Hissong, 1977). Conclusions were as follows:

1. Capital cost for air-blown gasifiers adequate for 1000 mw of capacity (3.5% S in coal) is on the order of $8 to $8.50 per kw.

TABLE 1

## COMPARISON OF COAL GASIFIERS TO PRODUCE REDUCING GASES

| | Koppers-Totzek | Winkler | Wellman[a] | Riley-Morgan | Wilputte |
|---|---|---|---|---|---|
| Type of coal bed | Entrained | Fluidized | Fixed | Fixed | Fixed |
| Feed coal size | 70 %<br>-200 mesh | 0 - ½" | ¼" - 1½" | ¼" - 1½" | ¼" - 1½" |
| Air or oxygen | Oxygen | Air[b] | Air[b] | Air | Air |
| Pressure, atmospheres | 1 | 1 | 1 | 1 | 1 |
| Temperature, °F | 2700-3300 | 1500-2200 | 900-1200 | 1200 | 850-950 |
| Produces tars and oils | no | no | yes | yes | yes |
| Product gas, mol % dry: | | | | | |
| CO | 56 | 21 | 28 | 28[c] | 28[c] |
| $H_2$ | 36 | 14 | 15 | 15 | 15 |
| $N_2$ | 1 | 55 | 51 | 51 | 51 |
| $CH_4$ | 0 | 3 | 2 | 2 | 2 |
| $CO_2$ | 7 | 7 | 4 | 4 | 4 |
| | 100 | 100 | 100 | 100 | 100 |
| Mol weight | 19.8 | 25.1 | 24.5 | 24.5 | 24.5 |
| Product gas (dry) yield: | | | | | |
| SCF/ton of dry coal | 65,000 | 142,000 | 114,000 | 116,000 | 119,000 |
| $H_2$ + CO (dry) yield: | | | | | |
| SCF/ton of dry coal | 59,800 | 49,700 | 49,020 | 49,880 | 51,170 |
| Commercial module, T/D of coal | 850 | 700 | 90 | 90 | 65 |

[a] Wellman-Galusha, Wellman-Incandes, McDowell-Wellman

[b] Can also be designed for oxygen (data herein valid only for air)

[c] Gas analysis assumed to be the same as for Wellman

## TABLE 2

## REQUIRED GASIFIER COAL CAPACITY FOR 1,000 MW COAL-FIRED POWER PLANT FGD

| | |
|---|---|
| Power plant output | 1,000 MW |
| Station heat rate | $10 \times 10^6$ Btu/MWH |
| Coal heating value | $24 \times 10^6$ Btu/ton |
| Coal sulfur | 3.5 wt % |
| Assumed conversion of coal sulfur to $SO_2$ | 100 % |
| Assumed FGD $SO_2$ removal | 90 % |

Boiler coal consumption
$= 1000(10 \times 10^6)(24)/24 \times 10^6 =$ 10,000 tons/day

Boiler coal sulfur
$= 0.035(10{,}000) =$ 350 tons/day

$SO_2$ removed in FGD
$= 350(64/32)(0.90) =$ 630 tons/day

$SO_2$ to be reduced to $H_2S$
$= 630(2/3) =$ 420 tons/day

REQUIRED GASIFIER COAL:

1 ton of $SO_2$ reduced requires[a]
$(2000/64)(3)(379) =$ 35,531 SCF $H_2$ + CO

| | SCF $H_2$ + CO per ton of dry gasifier coal[b] | T/D of dry gasifier coal required to reduce 420 T/D of $SO_2$ |
|---|---|---|
| Koppers-Totzek | 59,800 | 250 [1][c] |
| Winkler | 49,700 | 300 [1] |
| Wellman | 49,020 | 304 [4] |
| Riley-Morgan | 49,880 | 299 [4] |
| Wilputte | 51,170 | 292 [5] |

Notes:

[a] Based on stoichiometric hydrogen plus carbon monoxide required to reduce $SO_2$ with no credit for any methane or $H_2S$ present in reductant gas.

[b] See Table 1 for yield and composition of gasifier product gases.

[c] Number of gasifers required based on module sizes in Table 1 .

## TABLE 3

## GASIFICATION COSTS

BASIS: 1,000 MW power plant* at 75 % load factor
300 T/D of coal gasified in air-blown units
(Winkler, Wellman, Riley-Morgan, Wilputte)

| | | |
|---|---|---|
| CAPITAL INVESTMENT COST | $8,000,000 - $10,000,000 | |
| ANNUALIZED COSTS: | | |
| | $/year ($15/ton coal) | $/year ($30/ton coal) |
| Gasifier coal | 1,233,000 | 2,466,000 |
| Utilities | 70,000 | 70,000 |
| Labor | 288,000 | 288,000 |
| Capital related costs at 25 % per year | 2,225,000 | 2,225,000 |
| | 3,816,000 | 5,049,000 |
| mills/KWH of power plant output | 0.58 | 0.77 |

* As defined in Table 2 .

2. $SO_2$ inlet concentration has only a minor effect on capital cost.

3. Oxygen blowing increases investment by about 20%.

4. For annualized cost, $SO_2$ concentration also has a relatively minor effect (an increase of 0.05 mill per kw hr when the $SO_2$ is dropped from 85% to 25%). Oxygen blowing raised the cost by 0.14 mill.

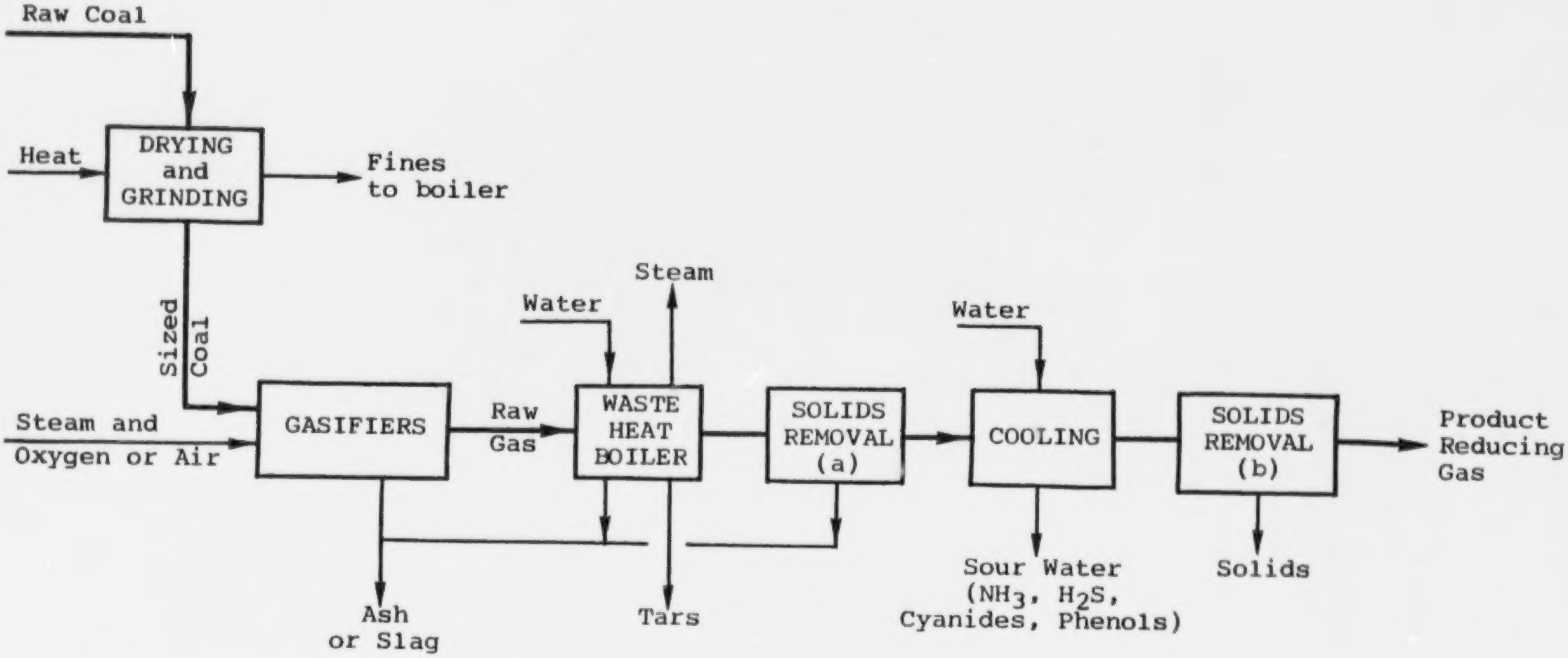
Figure 4 is a composite, conceptual flow diagram of the various gasifier systems as they might be adapted to the production of reducing gas for an FGD system. Since the gasifiers are not being used to produce a fuel gas, there is no need to remove $H_2S$ or organic sulfur for environmental reasons. Nor is there any requirement for shift conversion (of CO to $CO_2$) and removal of $CO_2$ to enhance the Btu content of the gasifier product gas. However, the product gas will need to be cleansed of any tars, oils, phenols and particulates. (The technical literature on coal gasification could well profit by a carefully defined study and design of the gas treatment sequence required to produce a cleansed reducing gas for application in FGD systems. The successful demonstration of such a design would be very helpful in the development of regenerable FGD systems.)

Heavy Oil Partial Oxidation (Radian, 1977; Gas Handbook, 1975)

The partial oxidation of heavy, residual fuel oil is a viable alternative to coal gasification in the production of reductant gas ($H_2$ + CO) for use in FGD systems.

There are two well-established, commercially proven partial oxidation processes, one offered by Texaco and one by Shell Oil. Both processes are non-catalytic and both were developed to provide synthesis gases for the subsequent production of hydrogen, ammonia, and methanol. The two processes are in operation at over 95 installations with a combined capacity of over two billion SCFD of hydrogen and carbon monoxide. On-stream factors of 95% or better have been achieved.

Table 4 presents the product gas composition and yield from a heavy oil partial oxidation unit using air (rather than oxygen). As noted earlier herein, the 1000 mw power plant FGD system defined in Table 2 requires 14.9 MM SCFD of reductant ($H_2$ + CO). Based on the yield in Table 4, this would require a partial oxidation feed rate of about 1,100 barrels/day of heavy oil. The capital investment and annualized costs for such a plant would be approximately:



(a) Cyclones or venturi scrubbers

(b) Electrostatic precipitator

COAL GASIFICATION
TO PRODUCE
REDUCING GAS

FIGURE 4

## TABLE 4

## FUEL OIL PARTIAL OXIDATION

| | |
|---|---|
| Type of oil | Fuel oil |
| Oil heating value (HHV) | 6,000,000 Btu/barrel |
| Air or oxygen | Air |
| Product gas, mol % dry: | |
| CO | 24 |
| $H_2$ | 15 |
| $N_2$ | 60 |
| $CH_4$ | negl |
| $CO_2$ | 1 |
| | 100 |
| Mol weight | 24.4 |
| Product gas (dry) yield: | |
| SCF/barrel of oil | 35,000 |
| $H_2$ + CO (dry) yield: | |
| SCF/barrel of oil | 13,650 |

- Capital investment = \$8,000,000-\$10,000,000
- Annualized costs = 1.0-1.1 mills/KWH of power plant output (assuming a 75% load factor)

Feedstock oil costs were assumed to be \$12 per barrel.

Figure 5 is a schematic flow diagram of a heavy oil partial oxidation plant. Single reactor modules are capable of producing 110 MM SCFD of reductant ($H_2$ + CO) from feed rates of 8,100 barrels per day. Thus, the requirements of a 1000 mw power plant FGD system would easily be accommodated within a single reactor module. After cooling in a waste heat boiler, the partial oxidation product gas is water-scrubbed free of soot and then cooled further. The soot is extracted from the resultant carbon-water slurry by a light oil (naphtha) and the resulting carbon pellets are recycled back to the reactor by being slurried (or homogenized) with the incoming oil feedstock.

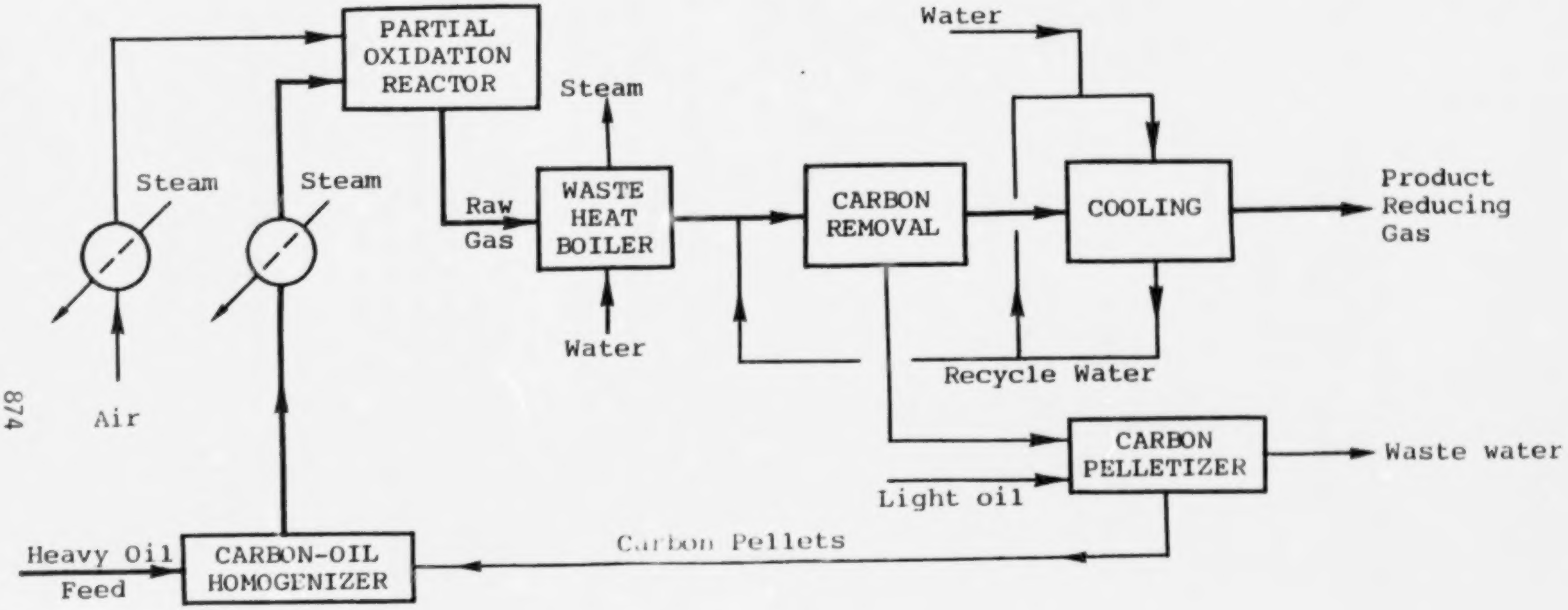
## Reduction of $SO_2$ to $H_2S$

Conversion of $SO_2$ to $H_2S$ is a fairly new practice, becoming significant with the advent of FGD systems. Three processes have been operated, one on a commercial basis (Allied Chemical) and two in test units (IFP and BAMAG).

Allied Chemical: Allied developed an $SO_2$ reduction process mainly for use in smelters and later used it on FGD systems. The reducing agent is methane which, as noted earlier, is not likely to be available for FGD use in the U. S. However, the process will be described since the operation is much like that when $H_2$/CO from a gasifier is used as the reducing agent.

Allied has installed the process at the Falconbridge smelter in Canada, the EPA FGD test facility (Wellman-Lord) at the Dean H. Mitchell station of Northern Indiana Public Service, and a full commercial FGD system (soon to start up) at the San Juan station of New Mexico Public Service. Descriptions have been given in several papers (Lakatos, et al., 1976; Hunter, 1973, Mann, et al., 1972; Bierbower and Van Sciver, 1974).

A simplified drawing of the system is shown in Fig. 6. A rich $SO_2$ stream (85-90%) from the Wellman-Lord process is mixed with natural gas and fed to the $SO_2$ reduction unit, a catalytic reactor-regeneration combination operated at a temperature above 1500° F. The incoming gas is heated and the exit gas cooled in two cyclic regenerators. Nearly half of the $SO_2$ is converted to sulfur in the reactor by direct reduction.



**HEAVY OIL
PARTIAL OXIDATION
TO PRODUCE
REDUCING GAS**

FIGURE 5

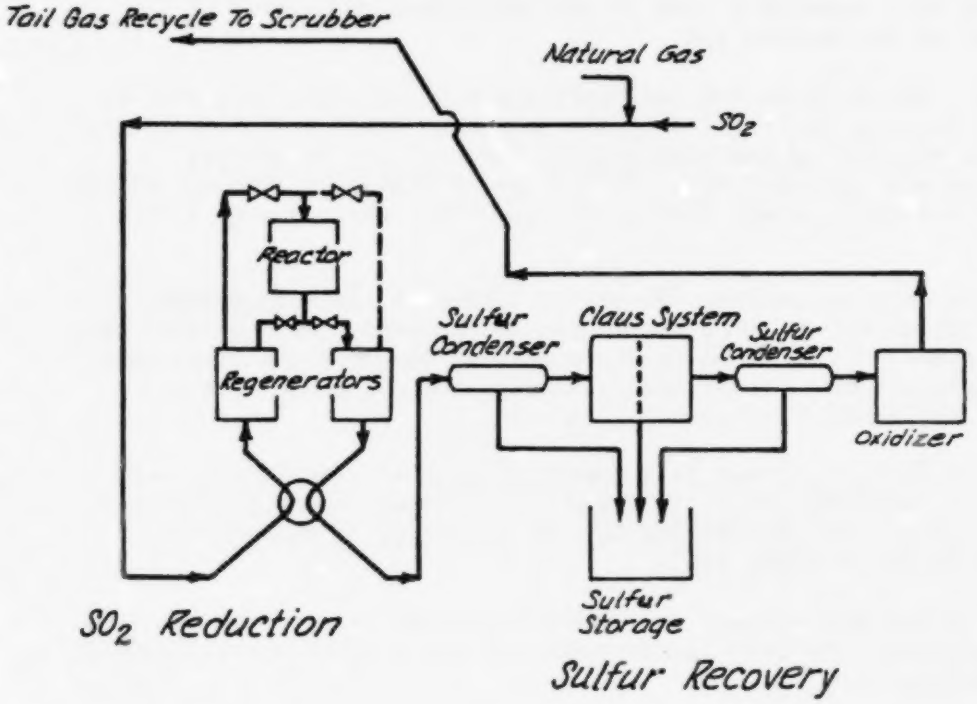


FIGURE 6

ALLIED CHEMICAL $SO_2$ REDUCTION PROCESS

The remainder is converted to the desired 2:1 $H_2S/SO_2$ mixture needed for the Claus reaction. A two-stage Claus is used. Unoxidized sulfur compounds are incinerated and recycled to the scrubber.

Capital cost projected for the process is about $9 per kw for a 500-mw system. This is for a unit treating a 100% stream of $SO_2$; at lower $SO_2$ concentrations, the cost increases rapidly, to about $11 at 40% $SO_2$ and $18 at 8%. Annualized cost is not applicable since much of it is in the cost of the natural gas.

IFP: In the 30-mw FGD test unit operated up until last year by IFP (Institut Francais du Petrole) at the Champagne station of Electricite de France, the $SO_2$ was reduced with a $H_2/CO$ mixture made by partial oxidation of natural gas with air. The system is basically like the Allied process described above except that a wet-type Claus unit is used (IFP design).

There were two reducer vessels in series in the test system, each packed with catalyst, but a single reducer probably would be used for a commercial plant. There is no sulfur condenser ahead of the Claus unit, since the single wet-Claus tower both completes the $SO_2$ conversion and condenses all the product sulfur.

The reducing gas feed is adjusted to give an $H_2S/SO_2$ mol ratio of about 2.2 in the Claus-inlet gas. The Claus-outlet concentrations are 1800 to 2600 ppm $H_2S$ and 300-600 ppm $SO_2$, representing an overall $SO_2$ conversion to sulfur of about 90%.

Costs are not relevant at Champagne because natural gas was used as the raw material. The main significance is that a $H_2/CO$ mixture worked well as a reductant for $SO_2$.

BAMAG: The Bergbau-Forschung test unit at STEAG's Kellermann station produces a gas stream containing about 20% $SO_2$, which is treated in a BAMAG unit to produce sulfur. The reducing agent is town gas, containing about 60% $H_2$, 6% CO, and 26% $CH_4$ + $C_xH_y$.

The BAMAG is similar to the others in that a high-temperature reactor is followed by Claus reactors. The former is called a "burner", operated at about 1850° F and apparently without catalyst. From 60 to 70% of the $SO_2$ is converted directly to sulfur in this unit and condensed from the gas before it passes through the three Claus reactors in series.

The main problems are as follows (Knoblauch, 1976).

1. Impurities such as dust, chloride, and fluoride in the $SO_2$ stream must be removed to prevent damage to the Claus catalyst.
2. If the system must be shut down often, as may be necessary for a low-load boiler, the catalyst probably will have a life of only about two months.

Gas-Phase Claus Plant (Goar, 1975; personal communication, 1977)

The conventional gas-phase Claus plant design, as used for decades in literally hundreds of petroleum refineries and natural gas desulfurization plants, usually processes feedstock gases containing 20-90% $H_2S$ and essentially no $SO_2$. Such a plant is depicted in Figure 7. Since the Claus chemistry requires a reactant gas of 2/3 $H_2S$ and 1/3 $SO_2$ by volume:

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

and since the typical feedstock gas to the Claus unit contains no $SO_2$, the conventional Claus unit includes a reaction furnace wherein air is used to burn 1/3 of the $H_2S$ to $SO_2$ and to attain the sulfur conversion reaction temperature. The reaction product gases are then cooled (in a waste heat boiler or condenser) to remove molten sulfur. The residual gases are reheated and passed over a catalyst bed to produce more sulfur which is then condensed out. To achieve about 95-97% sulfur conversion efficiency, the plant requires 3 catalyst bed stages (converters) in addition to the front-end combustion and reaction furnace. The residual gas (tail gas) from the final condenser is passed through a coalescer to remove entrained, molten sulfur and then goes either to a thermal incinerator, or to a tail gas desulfurization unit (if required to meet environmental restrictions).

In the application being considered in this paper, the feedstock gas from the FGD unit would contain 20-90% $SO_2$ and no $H_2S$. The Claus chemistry requirement of 2/3 $H_2S$ and 1/3 $SO_2$ by volume would be met by reducing 2/3 of the $SO_2$ to $H_2S$ in the reduction unit (see Figure 1). Hence, the Claus plant has no need for the inlet reaction furnace to burn any of the feedstock gas. In fact, the feedstock gas from the reduction unit would probably be routed directly to the first stage catalytic converter, with provision for reheating if needed.

As noted earlier herein, the 1000 mw power plant FGD system defined in Table 2 recovers 630 tons/day of $SO_2$ which is equivalent to a Claus plant feedstock sulfur content of 315 tons/day. The capital investment cost for a gas-phase Claus plant of that capacity would be approximately \$5,000,000-\$6,000,000.

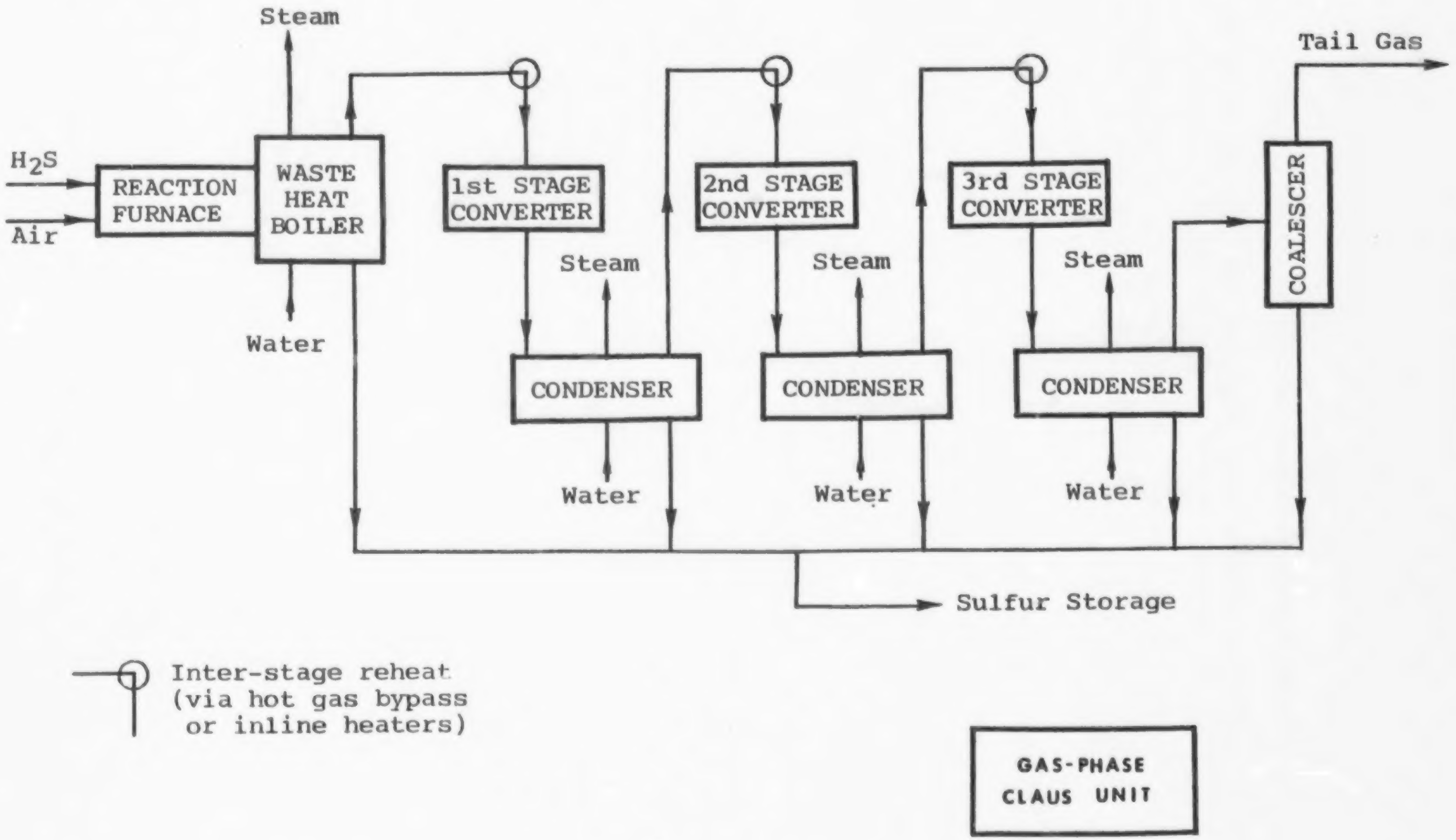

Steam
Tail Gas
$H_2S$
Air
REACTION FURNACE
WASTE HEAT BOILER
Water
1st STAGE CONVERTER
2nd STAGE CONVERTER
3rd STAGE CONVERTER
Steam
Steam
Steam
CONDENSER
CONDENSER
CONDENSER
Water
Water
Water
COALESCER
Sulfur Storage
Inter-stage reheat (via hot gas bypass or inline heaters)
GAS-PHASE CLAUS UNIT

FIGURE 7

## Liquid-Phase Claus Unit (Radian, 1977)

Figure 8 is a schematic flow diagram of the liquid-phase Claus reactor developed by IFP (Institute Francais du Petrole). The Claus chemistry is carried out at a relatively low temperature (about 300° F) in a catalyzed solvent. Product molten sulfur is withdrawn from the bottom of the packed tower reactor. The exothermic heat of reaction is removed and recovered from the circulating solvent. The desulfurized offgas from the reactor is sent to a thermal incinerator.

The catalyzed solvent is reported to be a polyethylene glycol solution containing a metal salt catalyst. IFP now has at least 20 units in commercial operation.

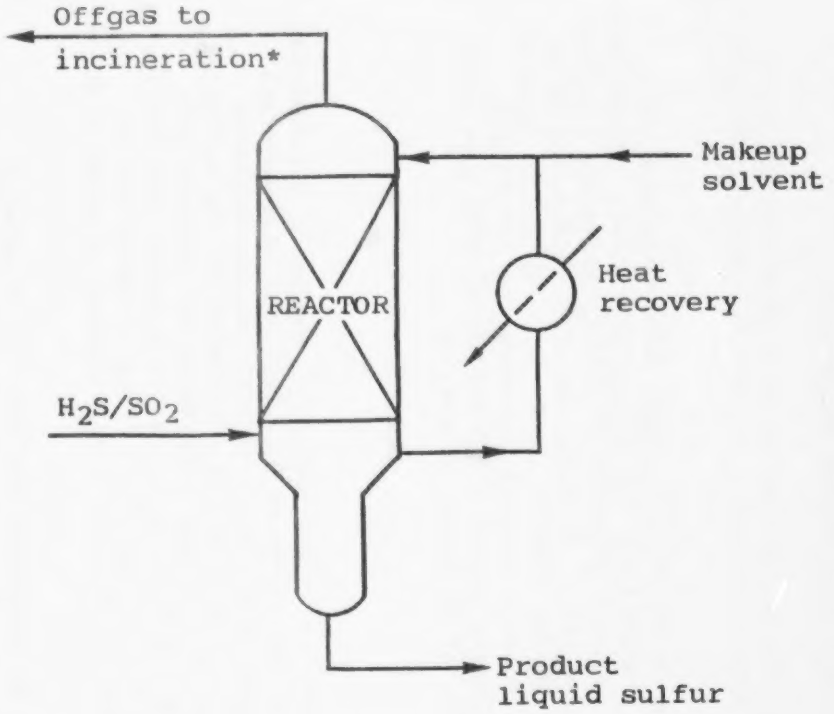
The IFP-1 process as depicted in Figure 8 was developed for processing tail gases from conventional gas-phase Claus units. It has been reported that such a plant processing 50 T/D of sulfur equivalent requires a capital investment of $3,000,000. Scaling that cost to the 315 T/D of sulfur equivalent required for the 1000 mw power plant FGD system (defined in Table 2) would give an estimated capital investment of $10,000,000, considerably more than the estimated cost of a conventional gas-phase Claus unit processing the same 315 T/D of sulfur equivalent.

## Economics of Sulfur

Whatever the process route for reduction, sulfur is a relatively expensive product for FGD in comparison to processes that give oxidized products such as sulfuric acid or ammonium sulfate. Recent estimates on overall cost, based on the same front end (Wellman-Lord) for scrubbing and $SO_2$ evolution, show a slightly higher investment for sulfuric acid (about $4 per kw for a 500 mw system) but a lower annualized cost (including capital charges) of about 0.45 mill per kw hr (roughly equivalent to $1.05 per ton of coal). This represents a cost reduction of about 7.3% by making sulfuric acid.

These figures are before credit for sale of the product. Sulfuric acid normally brings a higher sales revenue than for sulfur (about 65% higher in the above estimates) but marketing problems may offset much of this advantage. It must be concluded, however, that acid should have an advantage in most situations.

Ammonium sulfate, which is simpler to produce than either sulfur or sulfuric acid, should have even more of a cost advantage over sulfur. No cost estimates appear to be available for comparison. However, sulfate has the drawback of a more limited market than for acid and sulfur.



* If used in conjunction with FGD scrubbing with ammonia, offgas is cooled and sent to ammonia recovery before being incinerated.

**LIQUID-PHASE**
**CLAUS UNIT**

FIGURE 8

## Summary

Since there are several "front-end" processes that give a rich stream of $SO_2$ as an intermediate product, it is desirable to have an economical method for reducing $SO_2$ to sulfur, a more desirable product in several respects than sulfuric acid or ammonium sulfate. Petroleum-based materials such as natural gas or light oil fractions are the preferred reductants because of relatively low investment and simplicity of operation, but unfortunately are in short supply. Thus coal is the logical reducing agent.

Coal can be used either as a direct reductant, as in the RESOX process, or by gasifying it to give a $H_2$/CO mixture that can be used in a combination procedure--first reducing the $SO_2$ to an $H_2S/SO_2$ mixture and then converting this to sulfur by the standard Claus process. A considerable amount of direct reduction occurs in this technique also, but it is not practicable to go all the way, thus making the Claus step necessary.

Since RESOX involves only one step instead of three, the capital cost should be lower than for the gasification-Claus route. However, the method is not far enough along for definitive cost evaluation. The lower capital cost may be offset by the need to use a special and more expensive type of coal.

The main competition to RESOX may come from the ACP ("Aqueous Carbonate Process") in which coal is also used as the reductant but to reduce $Na_2SO_3/Na_2SO_4$ rather than $SO_2$.

A test of direct reduction with coal will be made in Europe. Gas from a coal gasifier has not yet been tested for $SO_2$ reduction but gases somewhat similar in composition have been used in two sizeable test units, also in Europe. Tests with coal gas appear warranted; the type of gasifier best suited for $SO_2$ reduction is one that is air blown and that operates at a high enough temperature to avoid tar and phenol production. The only purification necessary would be dust removal.

For FGD processes that give $SO_2$ as an intermediate, sulfuric acid may be a better product than sulfur. Production cost should be lower and sales revenue higher in most situations. However, sulfur has some major advantages in regard to marketability.

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# THE REDUCTION OF MAGNESIUM AND SODIUM SULFITES AND SULFATES

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## ABSTRACT

The reduction of the sulfites and sulfates of magnesium and sodium to elemental sulfur is a consideration in air pollution control processes both as a process option and as a means of regenerating magnesium and sodium compounds for recycle. The chemical basis for sulfate and sulfite reduction is considered in this paper. Both the thermodynamic and kinetic limitations are explored. A calculated process design for the production of elemental sulfur from magnesium sulfite/sulfate is given and discussed. The sodium system is more complex than the magnesium system.

It was concluded that both thermodynamic and kinetic considerations are important in either process. The magnesium salts require less reducing gas than the sodium system because the oxide rather than the sulfide is produced in the reduction step. The process temperature has a lower limit imposed by gas phase kinetics.

Sodium sulfite/sulfate reduction is more complex because of the extreme chemical stability of the sodium salts compounds. Sulfide formation occurs so that excess reductant is required. High temperatures are necessary because of solid and gas phase kinetics. The endothermic nature of the reaction requires that heat be added.

# THE REDUCTION OF MAGNESIUM AND SODIUM SULFITES AND SULFATES

## 1. INTRODUCTION

Several flue gas desulfurization (FGD) processes use magnesium or sodium compounds as process intermediates. For instance, in the magnesium oxide process the overall reaction scheme is:

Sorption: $MgO + SO_{2\,(dilute)} \rightarrow MgSO_3$

Regeneration: $MgSO_3 \rightarrow MgO + SO_{2\,(concentrated)}$

Overall: $SO_{2\,(dilute)} \rightarrow SO_{2\,(concentrated)}$

Examples of systems in which sodium compounds are intermediates include the Wellman-Lord and double alkali processes. Sulfite (sulfur in the +IV oxidation state, e.g., $SO_3^{-2}$, $HSO_3^-$, or $NaSO_3^-$) passes through the processes in some combination with the sodium ion.

Unfortunately some of the sulfites are converted to sulfates (sulfur in the +VI oxidation state, e.g., $SO_4^{-2}$, $HSO_4^-$, or $NaSO_4^-$). Because the sulfates of magnesium and sodium are more stable than the corresponding sulfites, special means must be provided for their removal from these cyclical processes.

Various options are available for the removal of sulfates from the cyclical process. Some of these are:

- purging and waste disposal,
- decomposition to sulfite or equivalent with the Mg (or Na) returned to the process,

- reduction to elemental sulfur with Mg (or Na) returned to the process.

At present most of the regenerative processes produce sulfuric acid. It would be of value to have the process option to produce elemental sulfur.

The EPA has addressed these questions for the magnesium oxide wet scrubbing process in work sponsored at Radian Corporation and reported by Lowell[1], et al. and Schwitzgebel and Lowell[2]. These reports contain several hundred references from the rather voluminous literature on the subject.

The chemical reduction of sodium sulfate, $Na_2SO_4$, to sodium sulfide, $Na_2S$, is a process that has been used commercially for decades. Pulping and paper industry experience[3] is of special interest. An air pollution control process with this molten salt reduction technology is presently being developed by Atomics International.

The objective of this paper is to present the underlying chemical principles for the decomposition and reduction of $MgSO_3$, $MgSO_4$, $Na_2SO_3$, and $Na_2SO_4$. The advantages and disadvantages of these processes can then be understood, and the difference between theoretical disadvantages and process inefficiencies may then be defined.

## 2.0 TECHNICAL APPROACH

The processes to convert sulfur from plus IV and VI to a lower oxidation state involve a reaction between a reducing gas and the solid or liquid sulfite or sulfate. There are two parts to the problem: the gas phase and the solid or liquid phase. First the gas phase will be discussed. Next will be the solid magnesium system, and finally the solid or liquid sodium system.

### 2.1 Gas Phase

The reducing gas can come from several sources. Typical reducing gases are mixtures of CO and $H_2$. Methane has also been used.

The actual reaction path is probably very complex. The initial reductant, $H_2$ for example, begins a reaction chain. Intermediates are formed that continue the reaction chain. Most reactions usually involve one or two reactants for each step on the path. The end products of interest are given in Table 1.

TABLE 1 GASEOUS SPECIES

Major or Minor

$H_2$
$H_2O$
$H_2S$
CO
$CO_2$
$S_2$
$S_8$

Minor or Trace

$CH_4$
COS
$CS_2$
$SO_2$
NaOH
Na
$S_3$
$S_4$
$S_5$

The reactions that involve the gas phase are gas/gas, gas/liquid, and gas/solid. When magnesium sulfite is heated it will decompose with or without the presence of reducing gas. It is therefore doubtful that gas/solid reactions play a significant role in the reduction of magnesium sulfite to elemental sulfur. On the other hand neither sodium sulfite or sulfate can be decomposed without the aid of a reducing gas. This indicates that gas/solid or gas/liquid reactions must be important.

Two aspects of gas/gas reactions will be considered: theoretical extent of conversion (thermodynamics) and kinetics. There are several items of interest concerning gas phase thermodynamics.

An interesting fact that has process significance is that sulfur has several possible forms in the gaseous state, i.e., $S$, $S_2$, $S_3$,$\cdots S_8$. A reaction to produce elemental sulfur in the gas phase will be used to illustrate this.

$$2H_2S + SO_2 \rightarrow 2H_2O + \frac{3}{x} S_x \qquad (1)$$

$S_8$ is the low temperature (t < 500 C) stable form while $S_2$ is the high temperature stable form. At 25°C the heat of reaction for Equation 1 to produce $S_8$ is exothermic at -26 Kcal. To produce $S_2$ it is endothermic at +11 Kcal.

This gives rise to the following results.

- The reaction to produce $S_8$ is exothermic with the theoretical extent of conversion decreasing with temperature.
- The reaction to produce $S_2$ is endothermic with the theoretical extent of conversion increasing with temperature.
- The combination of these two effects is a minimum in the theoretical extent of conversion at about 600°C.

Other competing reactions will respond in the same manner with respect to heat of reaction and extent of conversion. This means that as the temperature rises less heat will be given off, or if the reaction is already endothermic - more heat will have to be added.

From an equilibrium standpoint there are two significant points with respect to CO and $H_2$.

- CO has a greater affinity for oxygen than $H_2$.
- $H_2$ has a greater affinity for sulfur than CO. Thus, $H_2S$ is formed in preference to COS.

Kinetics are important in the gas phase. Generally speaking, the uncatalyzed gas phase reactions proceed rapidly above 700 to 900°C. Methane and sulfur dioxide do not react rapidly below 1200°C unless catalyzed. Catalysts can lower the reaction temperature - depending on the reaction - to 350-500°C. Some $H_2S/SO_2$ catalysts are effective to 150°C.

The significant aspects of reducing gas reactions are given below.

- An uncatalyzed gas phase process would have to operate at 900°C or higher.
- The reactions that produce elemental sulfur have a minimum in theoretical extent of conversion at about 600°C.
- CO is a better reductant (from theoretical extent of conversion) than hydrogen.

It is immaterial to the gas phase how the sulfur got there, i.e., from $MgSO_3$ or $Na_2SO_4$. Therefore the statements concerning gas phase reactions are valid for either solid. We now proceed to discuss the solids.

## 2.2 Magnesium Sulfite and Sulfate

It is convenient to approach the magnesium system by first looking at simple thermal decomposition of $MgSO_3$ or $MgSO_4$. Then reductive decomposition will be discussed. The following explanation of the decomposition of magnesium sulfite was given by Schwitzgebel and Lowell[2]. It is based first on the thermodynamics of what is possible and then on kinetics for limitations.

It was shown that $MgSO_3$ has a thermodynamic tendency to disproportionate.

$$4MgSO_3 \rightarrow MgS + 3MgSO_4 \qquad (2)$$

It was calculated that the vapor pressure of $SO_2$ above $MgSO_3$ is 1 atm at 360°C.

The sulfate of magnesium is more stable than the sulfite. It is, however, one of the least stable alkali or alkaline earth sulfates. It can be decomposed thermally at near 900°C. This can be shown quantitatively with thermodynamic calculations. An estimate of this can be made from thermodynamic quantities at 25°C.

The heat and Gibbs free energy of formation for the significant magnesium compounds are given in Table 2. From these data the heats and free energies of the decomposition reactions may be calculated. These are given in Table 3. The partial pressure of a single gas produced by the reaction may be calculated from the free energy change, $p = \mathrm{Exp}(-\Delta G/RT)$. This calculation has been made for the reactions in Table 3 that involve a single gaseous product.

The significance of the heats and free energies of these magnesium solids reactions is:

- disproportionation is thermodynamically favored,
- thermal decomposition of the sulfite occurs at low temperatures and is endothermic (requires heat),

### TABLE 2 THERMODYNAMIC PROPERTIES OF MAGNESIUM-SULFUR-CARBON-OXYGEN COMPOUNDS

| Compound | Formation Energies @ 25°C, Kcal/mole | |
|---|---|---|
| | $\Delta H_f$ | $\Delta G_f$ |
| MgO | -143.7 | -135.98 |
| MgS | -83.0 | -81.67 |
| $MgSO_3$ | -241.0 | -221.21 |
| $MgSO_4$ | -301.57 | -274.26 |
| $MgCO_3$ | -265.7 | -245.74 |
| | | |
| $SO_2$ | -70.95 | -71.74 |
| $SO_{3(g)}$ | -94.95 | -88.69 |

### TABLE 3 REACTION ENERGIES OF MAGNESIUM COMPOUNDS

| Reaction | Energy @ 25°C, Kcal | | Partial Pressure of Gas, atm |
|---|---|---|---|
| | ΔH | ΔG | |
| $MgSO_3 \rightarrow \frac{1}{4}MgS + \frac{3}{4}MgSO_4$ | -5.9 | -4.9 | - |
| $MgSO_3 \rightarrow MgO + SO_2$ | +26.4 | +13.5 | $1.25 \times 10^{-10}$ |
| $MgSO_4 \rightarrow MgO + SO_3$ | +62.9 | +49.6 | $4.2 \times 10^{-37}$ |

- thermal decomposition of the sulfate will occur at temperatures higher than those required for sulfite decomposition. Sulfate decomposition is more endothermic than sulfite decomposition.

Now kinetic effects will be considered. It would be expected from similar compounds (e.g., $CaSO_3$ and $Na_2SO_3$) that disproportionation kinetics are slow below 800°C. The vapor pressure of $SO_2$ above $MgSO_3$ is detectable at 200°C. Decomposition is rapid above 550°C. Thus the sulfite decomposes below the temperature where disproportionation could kinetically occur.

- This allows the option of thermal decomposition of $MgSO_3$ followed by reduction of the product gases ($SO_2$ and $SO_3$).

- The option is also available to use the exothermic reduction of $SO_2$ to provide heat for the endothermic decomposition of $MgSO_3$.

There are two related problems in producing elemental sulfur from a metal sulfite or sulfate: 1) separating the sulfur from the metal cation and 2) reducing the sulfur. Separating the sulfur from magnesium is no problem as was shown above. The solids will decompose to release $SO_2$. Process options may be investigated to do things such as trying to use the heat from the exothermic $SO_2$ reduction reaction to drive the endothermic $MgSO_3$ or $MgSO_4$ decomposition reaction.

One significant aspect of reducing the sulfur while it is in contact with the metal cation is the sulfide formation tendency. It is not desirable to reduce the sulfur past the zero valance state to the -II state. If the sulfur is reduced this far, it will then have to be oxidized back to the elemental state. This results in an extra expenditure of reducing gas. This is illustrated below for a metal cation, Me, being reduced with carbon monoxide.

Oxide Stable:

$$3CO + Me_xSO_4 \rightarrow Me_xO + 3CO_2 + S \tag{3}$$

or

Sulfide Stable:

$$4CO + Me_xSO_4 \rightarrow Me_xS + 4CO_2 \tag{4a}$$

$$Me_xS + \tfrac{1}{2}O_2 + CO_2 \rightarrow Me_xCO_3 + S \tag{4b}$$

Overall:

$$4CO + Me_xSO_4 + \tfrac{1}{2}O_2 \rightarrow Me_xCO_3 + S + 3CO_2 \tag{4c}$$

Notice how reduction to the sulfide required a threoretical reducing gas quantity of four moles CO per mole sulfate while the stable oxide required only three moles of CO. Sulfites have only three atoms of oxygen. Only two moles of reducing gas ($H_2$ or CO) are required to reduce a metal sulfite to oxide while three are required to reduce it to the sulfide.

The significant factors involved in the reduction of $MgSO_3/MgSO_4$ can best be seen by looking at a conceptual process design. First consider a low temperature process that would require gas phase reaction catalysts. A conceptual design of such a process is shown in Figure 1. Process design calculations were made for a fluid bed type calciner assuming all gas and solid species are in equilibrium. The detailed computational procedures were reported by Lowell[1] et al. The gas phases considered were given in Table 1. Solid phases considered are given in Table 4.

TABLE 4 SOLID PHASES CONSIDERED IN A MAGNESIUM SULFITE/SULFATE TO SULFUR PROCESS

$MgSO_4$

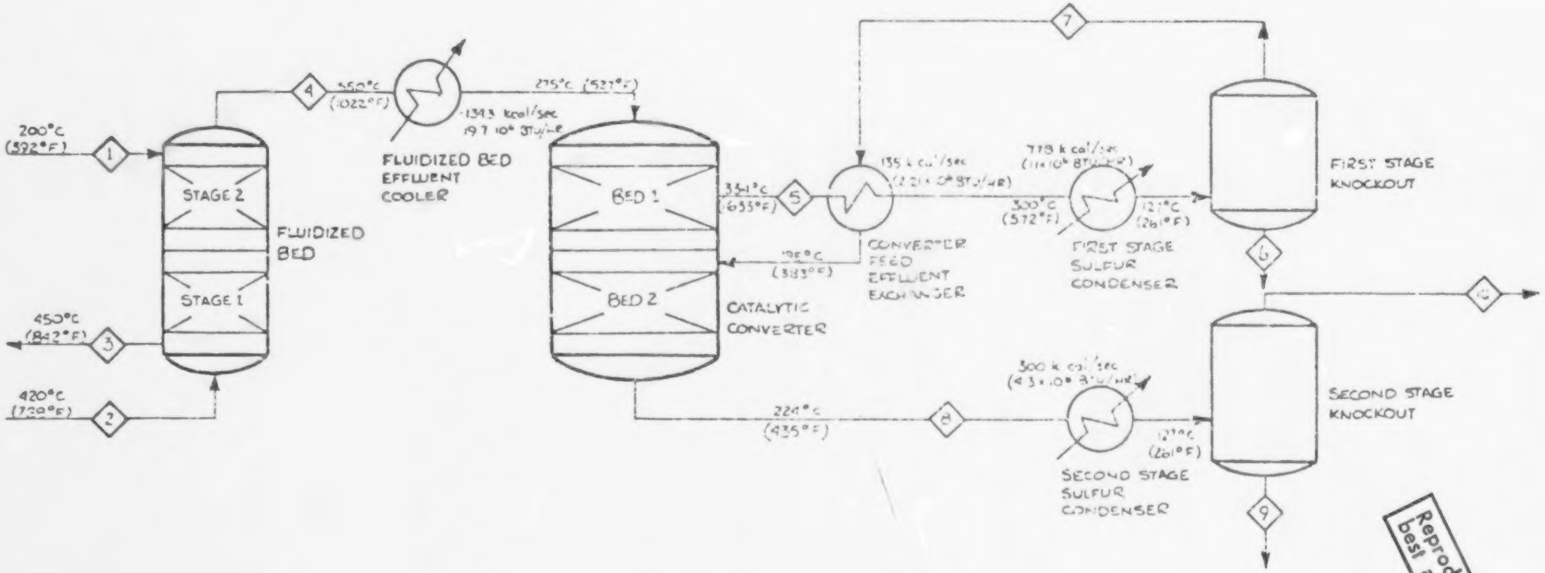
$MgSO_3$

$MgS$

$MgO$

$MgCO_3$

$C_{(graphite)}$



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| COMPONENT (g-moles/sec) | MW | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $N_2$ | 28.02 | | 155.33 | | 155.99 | 155.99 | | 155.99 | 155.99 | | 155.99 |
| CO | 28.01 | | 75.21 | | 0.04 | | | | | | |
| $CO_2$ | 44.01 | | 16.42 | | 98.11 | 99.16 | | 99.16 | 99.18 | | 99.15 |
| $H_2$ | 2.016 | | 45.32 | | 0.08 | | | | | | |
| $H_2O$ | 18.016 | | 24.96 | | 63.93 | 81.00 | | 81.00 | 88.01 | | 88.01 |
| $CH_4$ | 16.04 | | 7.55 | | | | | | | | |
| $NH_3$ | 17.03 | | 1.31 | | | | | | | | |
| $H_2S$ | 34.08 | | 2.30 | | 25.74 | 8.64 | | 8.64 | 1.63 | | 1.63 |
| $SO_2$ | 64.06 | | | | 13.12 | 4.34 | | 4.34 | .82 | | .82 |
| COS | 60.07 | | | | 0.37 | 0.02 | | 0.02 | | | |
| * Elem S | 32.06 | | | | 38.92 | 65.16 | 65.00 | .16 | 10.69 | 10.53 | .16 |
| $MgSO_3$ | 104.38 | 72.54 | | | | | | | | | |
| $MgSO_4$ | 120.38 | 3.31 | | | | | | | | | |
| MgO | 40.312 | | | 75.85 | | | | | | | |
| | | | | | | | | | | | |
| TOTAL | | 75.85 | 328.40 | 75.85 | 396.86 | 414.31 | 65.00 | 349.31 | 356.32 | 10.53 | 345.79 |
| MOL WT | | 105.08 | 24.19 | 40.312 | 32.40 | 31.04 | 32.06 | 30.48 | 29.87 | 32.06 | 29.81 |
| kg/sec | | 7.910 | 7.944 | 3.058 | 12.856 | 12.856 | 2.08 | 10.646 | 10.646 | .338 | 10.308 |
| Million lb/day | | 1.520 | 1.513 | 0.5824 | 2.450 | 2.450 | .397 | 2.45 | 2.45 | .0649 | 2.39 |
| * S g-atoms/molecule | | | | | 2.278 | 6.927 | 1.000 | 7.68 | 6.83 | 1.00 | 7.68 |

DRAWING NOTES:

1. STREAM COMPOSITIONS COMPUTED FROM EQUILIBRIUM CALCULATIONS AT 1.0 atm
2. BASIS FOR $MgSO_3$ FEED RATE:
   - 1000 MW POWER PLANT BURNING 2.3% SULFUR COAL
   - MAGOX SCRUBBING SYSTEM SULFUR REMOVAL EFFICIENCY: 90%
3. REDUCING GAS STOICHIOMETRY: 1.0
4. NO KINETIC LIMITATION ON CONVERSION OF INLET $MgSO_3$/$MgSO_4$ TO MgO ASSUMED

FIGURE 1. CONCEPTUAL PROCESS FLOW DIAGRAM FOR PRODUCING ELEMENTAL SULFUR FROM $MgSO_3$ IN A CATALYTIC DECOMPOSER

The $MgSO_3/MgSO_4$ feed composition was typical of that produced at Boston Edison's Mystic Station. The flow rate would approximate that of a 1000 Mw power plant burning 2.3 wt% sulfur coal with 90% $SO_2$ removal. A reducing gas typical of an air blown coal gasifier output was chosen at a 1.0 stoichiometry (stoichiometry based on reduction of sulfur to the zero valence state).

The significant features are:

- at the 550°C operating temperature the overall calcination/reduction reaction is still exothermic,
- MgO is the stable reduction product, not MgS,
- the conversion train to produce elemental sulfur from the fluid bed off gas is an overall heat producer,
- the process downstream of the reducing calciner is a small modification of "proven" technology,
- the reducing calciner is at present only a conceptual design and does not represent "proven" technology,
- conversion to elemental sulfur in a single step is not possible because of equilibrium constraints. A staged conversion is necessary.

Calculations were also made for a noncatalytic reducing calciner operating at 900°C and using a reducing gas typical of that produced in an oxygen blown coal gasifier. The calcination process is slightly endothermic as would be expected. MgO was still the stable product. The remainder of the system is very similar to the catalytic case.

## 2.3 Sodium Sulfite and Sulfate

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As shown by the formation energies in Table 5, sodium sulfite and sulfate are considerably more stable than the corresponding magnesium compounds. The formation energies (especially the free energy) of sodium oxide and sulfide are nearly the same. Note that the free energy of formation of MgO (Table 2) was significantly more negative than that of MgS. It can be anticipated that the tendency to form $Na_2S$ while reducing $Na_2SO_4$ will be significantly greater than the tendency to form MgS while reducing $MgSO_4$.

The potential of the sodium compounds to decompose may be determined from the reactions given in Table 6. The thermal decomposition of sodium sulfite to form $SO_2$ (as measured by vapor pressure) is more difficult than the decomposition of magnesium sulfate. Sodium sulfite also tends to disproportionate. Unlike magnesium sulfite which decomposes before disproportionating, sodium sulfite disproportionates first.

Sodium salts melt at lower temperatures than the corresponding magnesium compounds. The reducing gas is not kinetically active in attacking the very stable sodium sulfite or sulfate at temperatures below their melting point(s). This results in molten salts as part of the reduction process.

The various possible gaseous, liquid, and solid species make drawing conclusions from tabular thermodynamic data of limited value. Therefore, calculations were made to show how the equilibrium composition of products varies as a function of temperature and stoichiometry for a reducing gas with a $H_2/C$ ratio of two or zero. A total of 28 gas phase species was considered. The significant gas phase species were given in Table 1. The liquid and solid phase species considered are given in Table 7. Liquid species were assumed immiscible. The results of these calculations are presented in Table 8.

In comparing the amount of $Na_2SO_4$ remaining at a stoichiometry of 1.0 it is evident that a) low temperature favors the equilibrium reduction and b) carbon is a better reductant than hydrogen.

## TABLE 5 THERMODYNAMIC PROPERTIES OF SODIUM-SULFUR-CARBON-OXYGEN COMPOUNDS

| | Formation Energies @ 25° C (Kcal/mole) | |
|---|---|---|
| Compound | $\Delta H_f$ | $\Delta G_f$ |
| $Na_2O$ | -99.9 | -90.61 |
| $Na_2S$ | -89.0 | -86.37 |
| $Na_2SO_3$ | -260.4 | -242.96 |
| $Na_2SO_4$ | -331.55 | -303.38 |
| $Na_2CO_3$ | -270.26 | -250.50 |
| $CO_2$ | -94.05 | -94.26 |

## TABLE 6 REACTION ENERGIES OF SODIUM COMPOUNDS

| | Energy @ 25° C, Kcal | | |
|---|---|---|---|
| Reaction | ΔH | ΔG | Partial Pressure of Gas, atm |
| $Na_2SO_3 \rightarrow Na_2O + SO_2$ | 89.6 | 80.6 | $7.7 \times 10^{-60}$ |
| $Na_2SO_4 \rightarrow Na_2O + SO_3$ | 136.7 | 124.1 | $9.5 \times 10^{-92}$ |
| $Na_2SO_3 \rightarrow 1/4 Na_2S + 3/4 Na_2SO_4$ | -10.5 | -6.2 | -- |
| $Na_2CO_3 \rightarrow Na_2O + CO_2$ | 76.3 | 65.6 | $7.7 \times 10^{-49}$ |

## TABLE 7 LIQUID AND SOLID SPECIES CONSIDERED IN THE SODIUM SYSTEM

| Liquid | Solid |
|---|---|
| $Na_2SO_4$ | $Na_2SO_4$ |
| $Na_2S$ | $Na_2SO_3$ |
| $Na_2O$ | $Na_2S$ |
| NaOH | $Na_2O$ |
| $Na_2CO_3$ | $Na_2CO_3$ |
| | $C_{(graphite)}$ |

## TABLE 8 DECOMPOSITION OF SODIUM SULFATE

| Temperature, °C | 600 | | 1000 | | 1400 | 1000 |
|---|---|---|---|---|---|---|
| $H_2$/C Ratio | 2 | | 2 | | 2 | 0 |
| Stoichiometry[a] | 1.0 | 0.5 | 1.0 | 1.5 | 1.0 | 1.0 |
| Gas, Moles | 1.1309 | 1.1349 | 2.2699 | 3.8543 | 3.6954 | 1.5773 |
| Mole Fraction | | | | | | |
| CO | 0.0020 | Same as Stoichiometry 1.0 | 0.0271 | 0.1535 | 0.1205 | 0.3751 |
| $CO_2$ | .1125 | | .0606 | .0640 | .1490 | .3616 |
| COS | .0008 | | .0021 | .0023 | .0012 | .0732 |
| $H_2$ | .0262 | | .1284 | .3674 | .0951 | ------ |
| $H_2O$ | .5328 | | .4599 | .2456 | .3740 | ------ |
| $H_2S$ | .3252 | | .2924 | .1651 | .0260 | ------ |
| $SO_2$ | .0000 | | .0007 | .0000 | .0176 | .0003 |
| $S_2$ | .0003 | | .0277 | .0011 | .0241 | .1842 |
| $S_3$ | .0000 | | .0001 | .0000 | .0000 | .0019 |
| NaOH | .0000 | | .0006 | .0004 | .0906 | ------ |
| Na | .0000 | | .0002 | .0004 | .0992 | .0001 |
| Total | 0.9998 | | 0.9998 | 0.9998 | 0.9973 | 0.9964 |
| Phase | Solid | | Liquid | | Liquid | Liquid |
| Moles | | | | | | |
| $Na_2SO_4$ | 0.0156 | 0.5271 | 0.0554 | 0.000 | 0.1491 | 0.0000 |
| $Na_2S$ | .2453 | .0737 | .1474 | .3459 | .4985 | .2830 |
| $Na_2CO_3$ | .7391 | .3981 | .7962 | .6525 | .0000 | .7170 |

---

[a] Based on reduction to the sulfide.

The majority of cases presented are at 1000°C. Here it is seen that some $Na_2CO_3$ is stable. The amount of $Na_2S$ increases as the stoichiometry increases. Although some $Na_2CO_3$ is present, the $Na_2SO_4$ has not been totally decomposed even when enough reducing gas has been added to reduce all sulfur to the minus II state, i.e., sulfide. Another significant feature is that sodium species (NaOH and Na) appear in the gas phase in quantities that indicate possible operating problems.

At 1400°C two features are significant. The carbonate is no longer stable and the amount of gas phase sodium represents almost half of the original sodium.

Pure carbon was used as a reductant for comparative purposes. At 1000°C and a 1.0 stoichiometry the $Na_2SO_4$ is completely reduced. The majority of the sulfur is in the species $S_2$ with the balance in COS and liquid $Na_2S$. In comparing carbon to the hydrogen/carbon mixture, both at 1.0 stoichiometry, notice that carbon has reduced all of the $Na_2SO_4$ while $H_2/C$ has not. The gas phase of the carbon reduction has $S_2$, the desired end product, as the major sulfur containing species. The $H_2/C$ mixture has $H_2S$ as the major gaseous sulfur containing species. This illustrates the superior thermodynamic properties of carbon over hydrogen as a sulfur oxide reductant: carbon has a greater affinity for oxygen and a lesser affinity for sulfur than does hydrogen.

Thermodynamic calculations indicate what is possible. Kinetic limitations must be considered to predict what actually happens. The thermodynamic calculations of Table 8 indicate 600°C as a reasonable condition. The rate of the gas phase reactions is too slow to proceed uncatalyzed at this temperature (discussed in the $MgSO_4$ section). In addition, the solid $Na_2SO_4$ would not decompose to release $SO_2$ or $SO_3$. Thus there would have to be a gas phase attack upon the solid $Na_2SO_4$ that in practice does not occur.

At 1000°C most of the uncatalyzed gas phase reactions are kinetically active. The solid phase has been replaced by a kinetically more active liquid phase. The reaction is endothermic so that energy must be supplied at this temperature by combustion of excess reducing gas. Combustion (and not heat transfer) is the only practical means of supplying this high temperature heat.

The presence of sodium in the vapor phase has been noted in the paper industry. It has been stated[3] that this is vapor phase $Na_2SO_4$. The calculations presented here support the existence of significant vapor phase sodium, but indicate it to be in mainly the form of NaOH or Na.

## .0 SUMMARY AND CONCLUSIONS

Magnesium and sodium sulfite and sulfate may all be reduced to elemental sulfur. Gas phase kinetics are slow enough below 900°C (1650°F) that catalysts will be necessary. Magnesium sulfite and sulfate are reduced to the oxide plus gaseous products. The sodium salts are reduced to the sulfide, or more exactly, enough reductant must be added to reduce sulfur to the sulfide.

Magnesium salts are less stable than their sodium counterparts. The magnesium salt/gas phase reactions can take place at temperatures approaching 400°C (752°F). Sodium salts melt before significant solid/gas phase reactions take place.

The sodium salts are considerably more stable than magnesium salts as is evidenced by the fact that a magnesium reducing calciner is exothermic whereas the sodium salt reduction is endothermic.

It is concluded that both magnesium and sodium salts may be reduced to elemental sulfur. The extreme stability of sodium salts make them a less desirable choice than magnesium salts and a poor choice under any circumstance because of the

- amount of reductant required to produce the equivalent of a sulfide,

- amount of excess reductant to supply heat of reaction, and

- hostile chemical environment of high temperature, reducing conditions, and molten salts.

The magnesium salts require less reductant for reaction stoichiometry for oxide production and no excess reductant to supply heat of reaction. From a chemistry point of view they are a superior starting point for elemental sulfur production.

## ACKNOWLEDGEMENTS

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# PROCESS ALTERNATIVES FOR STACK GAS DESULFURIZATION WITH STEAM REGENERATION TO PRODUCE $SO_2$

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## ABSTRACT

New and existing processes are reviewed for stack gas desulfurization by aqueous scrubbing with steam regeneration to produce concentrated $SO_2$. H. F. Johnstone developed the basic concepts of simple absorption/stripping in the 1930s. His potential innovations to reduce steam consumption included: (1) reduced scrubber temperature, (2) the use of buffered solutions, (3) weak bases as buffers, and (4) insoluble acids as buffers. Ethylenediamine is identified in this paper as a potentially attractive weak base. Citric acid has recently been proposed as an attractive weak acid buffer. Glyoxalic acid is a unique aldehyde absorbent currently being proposed.

The only commercial example of steam regeneration, the Wellman-Lord process, crystallizes, $Na_2SO_3$ solids during stripping. This basic concept is expanded to include the crystallization of other types of solids. Methylammonium sulfite, ethylenediamine sulfite, $K_2S_2O_5$, and $K_2HPO_4$ are identified as solids that could be crystallized during steam regeneration. The alternatives for the buffer systems are evaluated not only in terms of steam requirements but also in terms of their effects on the ease and cost of removing sulfate impurities from the system. The numerous alternatives are structured to highlight attractive combinations.

# PROCESS ALTERNATIVES FOR STACK GAS DESULFURIZATION WITH STEAM REGENERATION TO PRODUCE $SO_2$

## INTRODUCTION

Aqueous scrubbing with steam stripping or evaporative crystallization has received attention as a method of desulfurizing stack gas with the production of concentrated $SO_2$. The $SO_2$ product is suitable for conversion to sulfuric acid or elemental sulfur. The market for these products should be adequate, unless there is a major change in the current trend of utilities to select mostly throwaway processes for flue gas desulfurization. Even so, credit for product sales will be only a small portion of the total process cost. Furthermore, adoption of regenerable processes necessarily commits the user to chemical processing and marketing activities, unless an outside party is hired to operate the pollution control facility. Steam regeneration is attractive because it can be combined with further processing to make a marketable product (sulfuric acid) without using a reductant while operating at relatively low temperature.

The earliest work on steam regeneration was done by H. F. Johnstone in the 1930's (Johnstone, 1935; Johnstone et al, 1938). He explored alternative aqueous absorbents such as alkali sulfite/bisulfite and organic acid buffers in a flowsheet utilizing simple absorption/stripping. The only significant commercial example of steam regeneration is the Wellman-Lord process (Davis, 1971; Schneider and Earl, 1973). It absorbs $SO_2$ in a sodium sulfite solution which is regenerated by evaporative crystallization to give concentrated $SO_2$ and $Na_2SO_3$ solids.

The process alternatives for steam regeneration include variations in both flowsheet configuration and selection of the aqueous absorbent. Except for the Wellman-Lord process, most of the processes of current interest use simple absorption/stripping. The absorbents being proposed include sodium citrate (Nissen et al, 1976), glyoxalic acid (Stark et al, 1976), and ammonium sulfite (Slack and Hollinden, 1975). The important factors affecting the economic and environmentally-acceptable application of steam regeneration processes are steam requirements, sulfate removal and disposal, process complexity, and absorbent cost.

The purpose of this paper is to structure these existing alternatives for steam regeneration and to generate and explore new processing alternatives which may be logically derived from the existing set. The alternatives will be presented as evolutionary improvements to the simplest possible case, simple absorption/stripping with sodium sulfite/bisulfite solution. More detail on this work is given by Rochelle (1977), who also makes a similar analysis of aqueous scrubbing processes with throwaway products (summarized by Rochelle and King, 1977a) and with $H_2S$ regeneration (summarized by Rochelle and King, 1977b).

## SIMPLE ABSORPTION/STRIPPING

The most general flowsheet option for aqueous scrubbing with steam regeneration is given in Figure 1. Hot flue gas is prescrubbed with water to remove HCl, $SO_3$, residual flyash, and possibly $NO_2$.

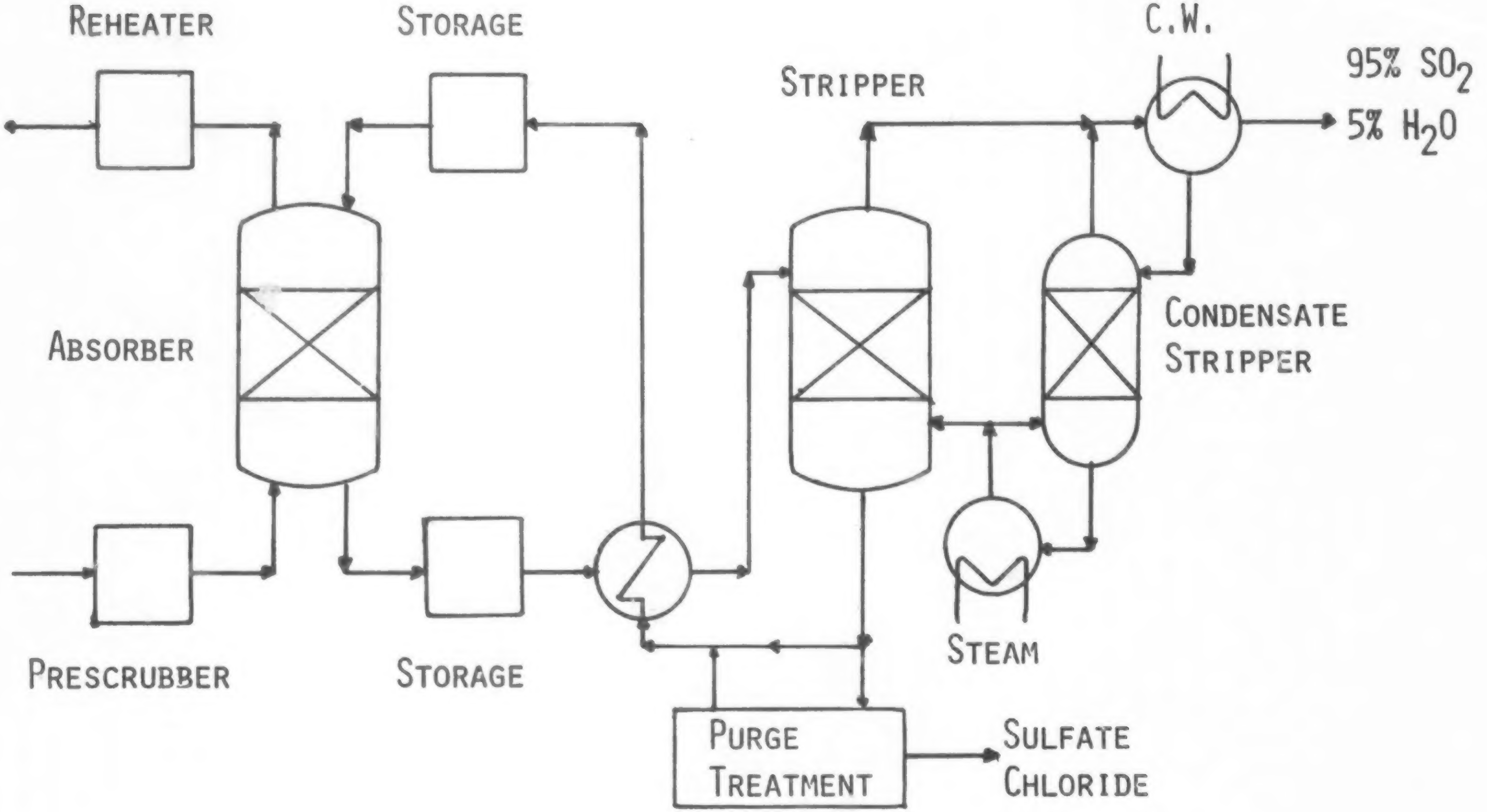

Figure 1. Simple absorption/steam stripping

$SO_2$ is removed by an aqueous solution at 50-60°C in a countercurrent absorber with 10-20 feet of packing or 3-6 trays. The lean and rich solutions are cross-exchanged for optimum heat recovery. Intermediate storage of the lean and rich solutions permits decoupling of scrubber operation from solution regeneration. The $SO_2$-rich solution is stripped with live steam at 90-100°C in a countercurrent packed or tray column. Water is condensed from the stripper overhead, stripped with a small amount of steam in a separate column, and vaporized to produce live steam for the main stripper. The $SO_2$ product is normally a gas containing about 95% $SO_2$ and 5% $H_2O$. It would be converted by further processing to sulfuric acid, liquid $SO_2$, or elemental sulfur. Continuous purge treatment is necessary to remove any accumulation of sulfate or chloride from the scrubbing solution.

Three general types of aqueous absorbents have been proposed for use with this flowsheet - buffers, alkali sulfite/bisulfite and aldehydes. Buffers in the pH range of 4 to 7, such as sodium citrate, provide for reversible $SO_2$ absorption as bisulfite by instantaneous acid/base reaction:

$$SO_2(g) + H_2O \rightleftarrows HSO_3^- + H^+$$

In a well buffered solution the $SO_2$ partial pressure will be proportional to total dissolved $SO_2$. Alkali sulfite/bisulfite solution is a special case of buffers where the net absorption reaction is given by:

$$SO_2(g) + SO_3^= + H_2O \rightleftarrows 2HSO_3^-$$

In this case, the $SO_2$ vapor pressure is a nonlinear function of total dissolved $SO_2$ as given by:

$$P_{SO_2} = K \frac{[HSO_3^-]^2}{[SO_3^=]}$$

Aldehydes such as glyoxalic acid absorb $SO_2$ reversibly at low pH as a hydroxysulfonate (Green and Hine, 1974):

$$RC{=}O + SO_2 + H_2O \rightleftarrows RCOH\text{-}SO_3^- + H^+$$

Because pH is not constant, the $SO_2$ vapor pressure will be a nonlinear function of $SO_2$ absorption.

Absorber/stripper design and performance for most steam regeneration alternatives is dominated by liquid/vapor equilibrium. Four simplifications can be made to idealize system steam requirements:

1. Assume an infinite number of stages or infinite height of packing in the absorber and stripper.
2. Assume perfect cross-exchange of the lean and rich solutions.
3. Assume a linear equilibrium relationship.
4. Assume no change of the ratio of $H_2O$ to $SO_2$ vapor pressures with temperature.

Under these conditions the amount of steam required in the stripper is equal to the total amount of water vapor contained in the saturated flue gas. In other words the ratio of $H_2O$ to $SO_2$ in the stripper overhead is equal to the ratio of $H_2O$ to $SO_2$ in inlet flue gas saturated to water. Thus a typical flue gas containing 2000 ppm $SO_2$ and saturated with 15% $H_2O$ would require about 75 moles steam/mole $SO_2$ for steam stripping. Note with these simplifications that the level of $SO_2$ removal does not affect steam requirements.

In practice a finite number of contacting stages must be used in the absorber and stripper. Depending on the relative costs of steam and equipment, this consideration would increase steam requirements by a factor of 1.2 to 1.5. The optimum number of stages would also be directly related to the required level of $SO_2$ removal.

The assumption of perfect cross-exchange results in a system where the steam requirements are independent of solution capacity for $SO_2$ absorption. In practice the solution capacity for $SO_2$ absorption should be greater than 0.05-0.10 moles/liter in order to minimize the size and cost of cross-exchange. With acid/base absorption of $SO_2$ this criteria implies a solution of pH greater than 4-4.5. With high solution capacities the assumption of perfect cross-exchange is generally acceptable.

The sodium sulfite/bisulfite system gives a highly nonlinear equilibrium relationship of liquid and gas $SO_2$ concentrations. As a result, in an optimized system gas and liquid are nearly at equilibrium in the top and bottom of the absorber and the middle of the stripper and far from equilibrium in the top and bottom of the stripper and the middle of the absorber. Ideally, the approach to gas/liquid equilibrium should be about the same throughout the absorber and stripper. At 90% $SO_2$ removal in the absorber, the nonlinearity of sodium sulfite/bisulfite equilibria increases the steam requirements by a factor of 1.5. At 97% $SO_2$ removal, nonlinearity increases the steam requirements of this system by a factor of 3.0. Steam requirements vary with $SO_2$ removal in the absorber because it becomes increasingly more difficult to strip $SO_2$ from the scrubber feed. As $SO_2$ is stripped from sulfite/bisulfite solution, the pH increases and the next increment of $SO_2$ is even more difficult to remove.

Johnstone found for most solutions of weak acid buffers or alkali sulfite/bisulfite that the ratio of $H_2O$ to $SO_2$ vapor pressure was only a weak function of temperature (Johnstone, 1935; Johnstone et al, 1938). Therefore, the fourth simplification is valid when scrubbing with sodium sulfite/bisulfite solution. As a result steam requirements with sodium sulfite/bisulfite solution will be 1.8 to 2.2 times more than the ratio of $H_2O$ to $SO_2$ in the scrubber inlet, because of the need for finite contactors and the nonlinearity of the absorption stripping equilibria.

## Gas Cooling

The steam requirements of a simple absorption/stripping process with any aqueous absorbent can be reduced by scrubbing at temperatures below the adiabatic saturation temperature of the flue gas. This would be achieved by direct or indirect nonadiabatic cooling of the flue gas. Reduced scrubbing temperature results in a lower concentration of $H_2O$ in the flue gas and thereby reduces the ratio of $H_2O$ to $SO_2$ vapor pressure in the solution from the absorber. As a result, with weak acid buffers or alkali sulfite/bisulfite, absorber cooling from 55°C to 35°C will reduce steam requirements almost a factor of three. Gas cooling may also enhance the rates of $SO_2$ mass transfer and reduce the volatility of solution components such as $NH_3$ and organic acids.

Such a concept has been practiced by the Russians at Niiogaz. They cooled the flue gas to 35°C by direct contact with once-through cooling water which was neutralized and disposed of. $SO_2$ was absorbed by ammonium sulfite/bisulfite solution. With an inlet $SO_2$ gas concentration of 3000 ppm, the steam requirement for stripping was 27 moles $H_2O$/mole $SO_2$ (Slack and Hollinden, 1975).

Commercial practice in the U.S. would not allow for direct contact cooling with disposal of waste water. Cooling would probably be achieved, as in Figure 2, by direct countercurrent contact of flue gas with cold recirculating solution. The recirculating solution would be indirectly cooled by water in a heat exchanger made of corrosion-resistant materials such as Incoloy 625. The temperature driving force available for heat exchange could be increased by permitting high concentrations of soluble additives such as $CaCl_2$ to accumulate in the recirculating solution. Clearly, such a cooling system would not be inexpensive nor maintenance-free. Therefore, non-adiabatic gas cooling is an alternative for reducing steam requirements that has not generally been exploited.

### Alleviating Equilibrium Nonlinearity

Steam requirements could be reduced as much as 35% by alleviating the nonlinear characteristics of the gas-liquid equilibrium of sodium sulfite/bisulfite solution. Johnstone recognized the value of using an additional buffer to give a more nearly linear equilibrium relationship. At a constant pH in the range of 4-6, his data show that $SO_2$ vapor pressure is directly proportional to total dissolved $SO_2$:

$$P_{SO_2}=K\cdot 10^{-pH}[SO_2]_T$$

$$K_{50^oC}=60\text{atm }\overline{M}^{-2}$$

Thus a solution buffered at a constant pH would give a linear equilibrium relationship. Johnstone (1935) tested phosphate buffer. The Bureau of Mines and Peabody have tested sodium citrate buffer. Other potentially-effective buffers include phthalate, adipate, and succinate (Rochelle, 1977).

With a sulfite/bisulfite buffer, the effect of nonlinearity can also be essentially eliminated (at 90% $SO_2$ removal) by using a split

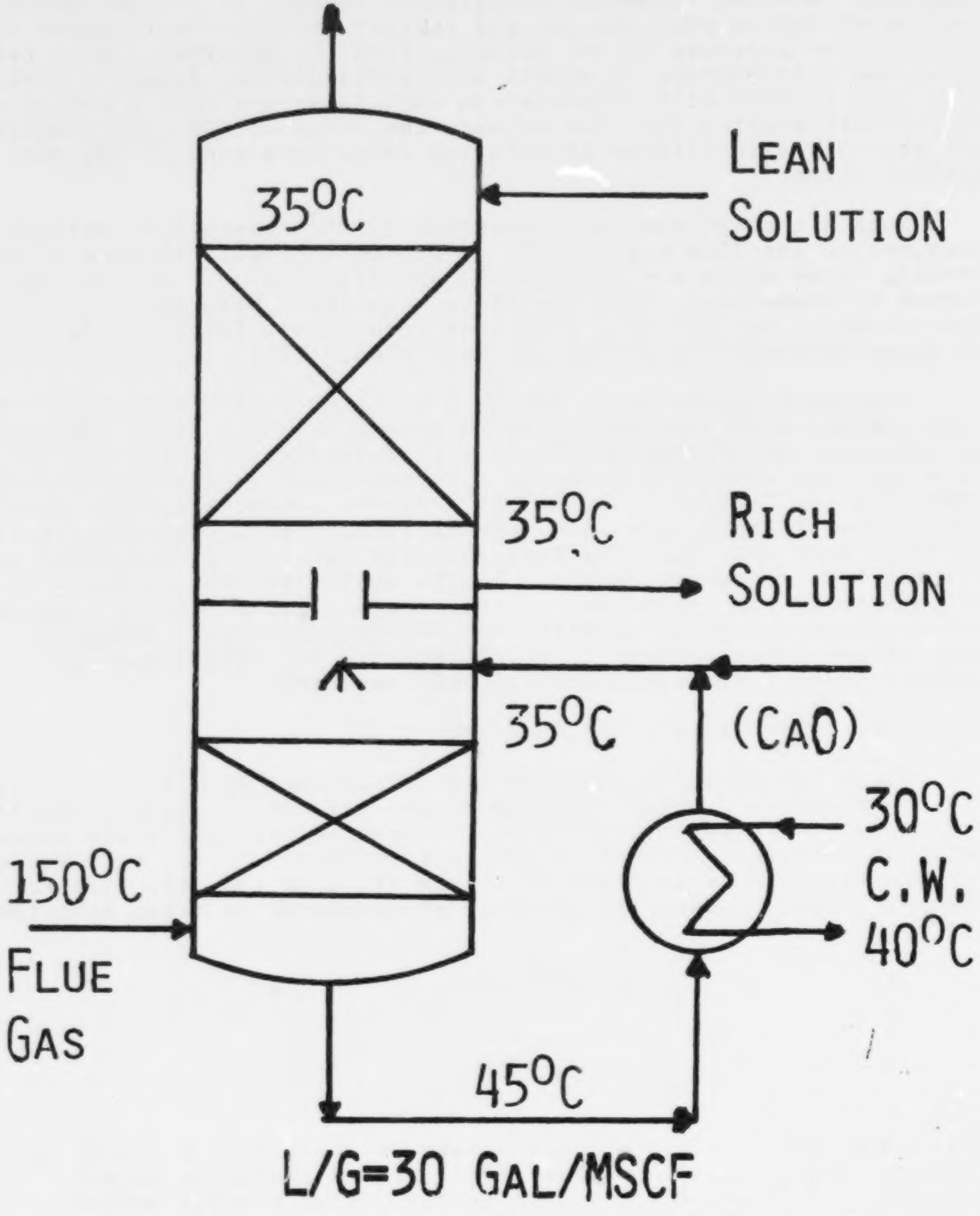

Figure 2. Nonadiabatic gas cooling

feed to the absorber as in Figure 3. Solution is withdrawn from the middle of the stripper and fed to the middle of the absorber. Thus, there is a higher rate of liquid circulation through the bottom of the absorber and the top of the stripper, where the pH and solution capacity is generally lower. This flowsheet is generally used in absorption/stripping systems for $CO_2$ concentration (Kohl and Riesenfeld, 1960).

## Temperature Effects

Johnstone (1938) found for most weak acid buffers and sulfite/bisulfite solutions that the ratio of $SO_2$ to $H_2O$ vapor pressure was only a weak function of temperature. Steam requirements for stripping will be lower if the ratio of $SO_2$ to $H_2O$ vapor pressure increases with temperature. Table 1 gives the factor by which this ratio increases in going from 55°C to 100°C for several absorbent solutions. For sulfite/bisulfite solutions, the factor varies from 0.84 ($Na^+$) to 1.15 ($NH_4^+$). The systems using $NH_4^+$ and $CH_3NH_3^+$ give a somewhat greater temperature factor because they have some weak base characteristics. The temperature factors for weak acid buffers appear to be in the range of 0.9 to 1.4.

Johnstone recognized that weak base buffers such as dissolved aluminum and aromatic amines give higher temperature factors, in the range of 1.8 to 5.8 for 55°C to 100°C. The $pK_a$ values of these buffers decrease rapidly with temperature. Therefore, the pH of a given solution will decrease with heating, thereby increasing the $SO_2$ vapor pressure. Aniline and other aromatic amines such as toluidine (Weidmann and Roessner, 1936) and dimethylaniline (Fleming and Fitt, 1950) have been proposed for and used in absorption/stripping systems at low gas temperature (25°C). However, their volatility makes them unacceptable alternatives for use with large gas volumes at 55°C. $Al_2(SO_4)_4$ and $AlCl_3$ solutions are effective only at pH less than 4-4.5 because of the limited solubility of aluminum hydroxide and basic aluminum sulfate at higher pH. Therefore, to get adequate solution capacity the flue gas must be scrubbed at 30-40°C. Nevertheless, with flue gas cooling the steam requirements of systems using these solutions would be quite attractive. The polyamines, ethylenediamine and diethylenetriamine, were briefly characterized by Roberson and Marks (1938). They should be nonvolatile under scrubber conditions because of the multiple hydrophilic groups which will usually be partially protonated. Ethylenediamine has a first $pK_a$ value of 7.0 at 20°C which decreases to 6.07 at 60°C and 5.34 at 100°C (McIntyre et al, 1959). It is therefore suitable for use at 50-60°C, especially if dissolved chloride or sulfate is allowed to accumulate so that the stripped solution at pH 6 contains little dissolved sulfite.

Johnstone also recognized that systems containing acids as separate liquid or solid phases could give greater temperature factors. If the acid is more soluble at higher temperatures it will dissolve and thereby reduce the pH of the solution as it is heated. The reduced pH increases $SO_2$ vapor pressure. Johnstone (1938) identified valeric acid as a possible alternative, but it is too volatile for

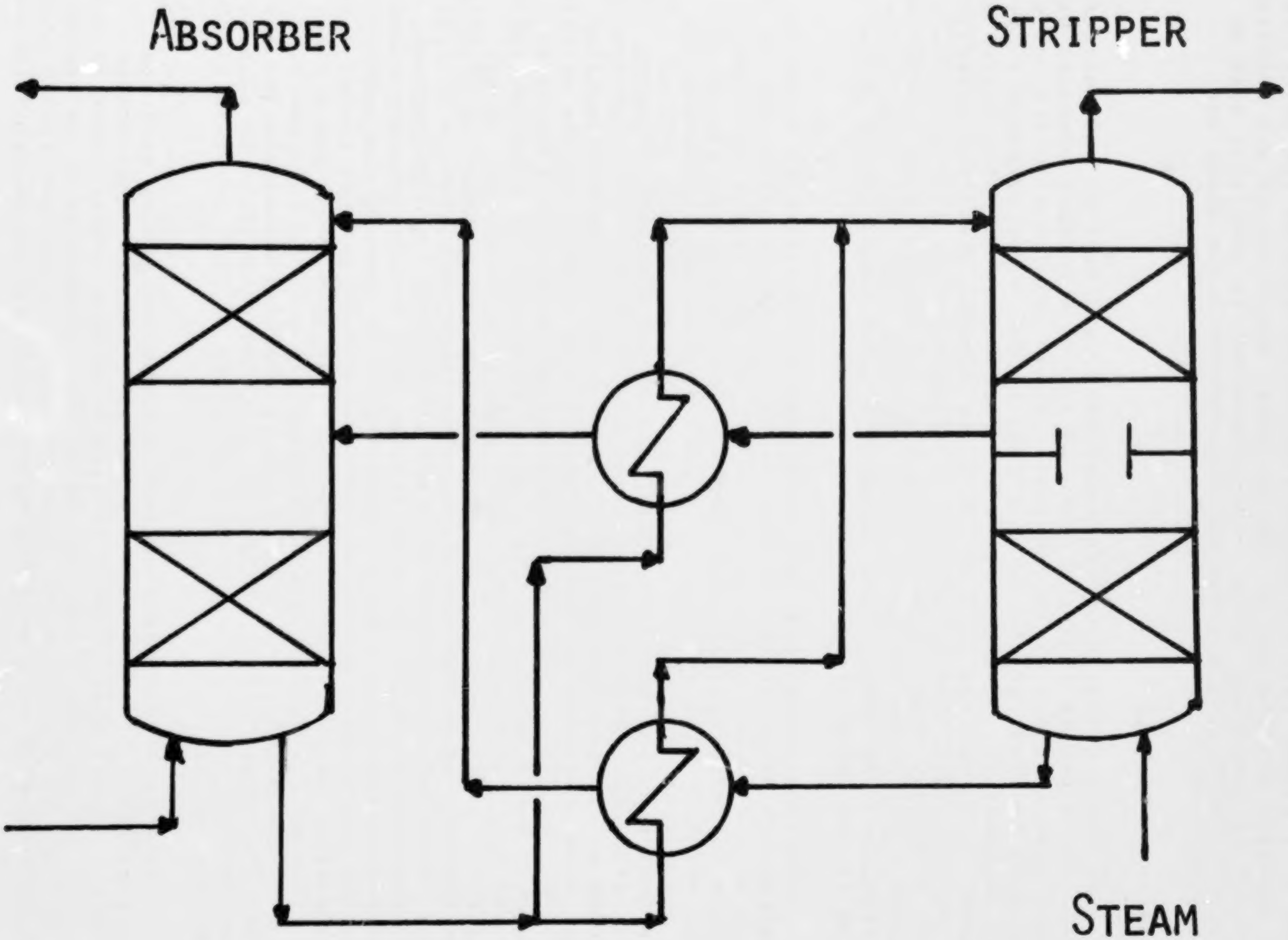

Figure 3. Split scrubber feed

Table 1: TEMPERATURE FACTORS

| Absorbent | $\frac{(P_{SO_2}/P_{H_2O})_{100°C}}{(P_{SO_2}/P_{H_2O})_{55°C}}$ | Reference |
|---|---|---|
| Sulfite/bisulfite | | |
| $Na^+$ | 0.84 | Johnstone et al, 1938 |
| $K^+$ | 1.01 | Linek and Hala, 1967 |
| $NH_4^+$ | 1.15 | Johnstone, 1935 |
| $CH_3NH_3^+$ | 1.10 | Johnstone et al, 1938 |
| Monethanolamine | 0.7-1.2 | Roberson and Marks, 1938 |
| Ethylenediamine | 1.1 | Roberson and Marks, 1938 |
| Weak Acid | | |
| Citrate, $Na^+$ | 0.9-1.4 | Rosenbaum et al, 1971<br>Oestreich, 1976 |
| Phosphate | 1.0-1.2 | Johnstone, 1935 |
| Sulfosuccinate | 1.2 | Keller and Wiseman, 1950 |
| Weak Base | | |
| $Al^{+3}$, $Cl^-$ | 3.7 | Johnstone, 1935 |
| $Al^{+3}$, $SO_4^=$ | 1.8-3.0 | Applebey, 1937 |
| Aniline | 3.3 | Johnstone et al, 1938 |
| Ethylenediamine, $Cl^-$ | 6* | Rochelle, 1977 |
| Diethylenetriamine | 2.4-5.8 | Roberson and Marks, 1938 |
| Separate Acid Phase | | |
| Valeric | 1.8-3.2 | Johnstone et al, 1938 |
| Adipic, pH-4.5 | 5-6* | Rochelle, 1977 |
| $K_2S_2O_5$ | 5-6* | Rochelle, 1977 |
| $KH_2PO_4$ | 3.5* | Rochelle, 1977 |

*Estimated from $pK_a$ values and solubilities practical use. Adipic acid, $K_2S_2O_5$, and $KH_2PO_4$ are all acid solids whose solubilities increase rapidly with temperature. Careful design would be required to avoid the crystallization of the acid solids in the scrubber.

Aldehydes such as glyoxalic acid (Marcheguet and Garden, 1967) and glyoxal (Marcheguet, 1961) have totally different characteristics. The reversible reaction of $SO_2$ with an aldehyde is very sensitive to temperature. The temperature factor from 55° to 100°C of a typical aldehyde, such as benzaldehyde, will be 15-20 (Stewart and Donnally, 1932). Therefore, steam requirements are determined more by sensible heating than by stripping needs. The limitation of aldehydes is their lack of effectiveness at a normal scrubbing temperature of 50-60°C. In order to get sufficient solution capacity and/or adequate rates of mass transfer, developers of the process using glyoxalic acid have found it desirable to cool the flue gas to 35°C (Stark et al, 1976). In the future, other nonvolatile aldehydes may be identified which do not have this limitation.

## SOLUTION EVAPORATION

With a system configuration as in Figure 1, water condensed from the $SO_2$ product is used to produce live steam for the stripper. A more common arrangement proposed by system developers is indirect evaporation of the stripper bottoms solution to produce stripping steam. Condensate from the $SO_2$ product is usually returned to the top of the main stripper, thereby avoiding the need for a condensate stripper. This configuration is simpler than that of Figure 1, but requires an evaporator constructed of corrosion resistant material. Furthermore, under some conditions return of condensate to the stripper will significantly increase steam requirements.

If the amount of solution evaporated during regeneration is a large fraction of the total circulating solution, then the solution can be significantly more concentrated in the evaporator than in the rest of the system. In the extreme, such evaporation can result in the crystallization of sulfite, bisulfite, sulfate, or buffer salts. Furthermore, $H_2O$ condensed from the $SO_2$ product must be recycled to some point in the system where it will significantly dilute the working solution. The condensate can also be used to redissolve crystalized solids. As a result of concentration/dilution or crystallization/dissolution, the $SO_2$ vapor pressure can be significantly affected at the respective points in the system. In the absence of additional liquid or solid phases (besides aqueous solution and gas) or with the crystallization/dissolution of basic solids such as $Na_2SO_3$ or buffer salts,solution concentration will increase the $SO_2$ vapor pressure. Dilution by $H_2O$ condensate will reduce the $SO_2$ vapor pressure. With the crystallization/dissolution of acid solids such as $K_2S_2O_5$ or buffer acids, evaporative concentration will reduce the $SO_2$ vapor pressure, while $H_2O$ dilution will increase it.

These dilution/concentration effects can be effectively used to reduce steam requirements and/or the number of stages in the stripper. The Wellman-Lord process evaporates sodium sulfite/bisulfite solution with the crystallization of $Na_2SO_3$. The effect of concentrating the solution is so great that only one stage of evaporation/stripping is adequate to strip out the $SO_2$. Dilution water is used to make up scrubber feed solution by redissolving the $Na_2SO_3$ solids. The actual steam requirement is directly related to the solubility of the sulfite salt. Lower steam requirements could potentially be achieved by crystallizing more soluble sulfite salts such as ammonium sulfite or methylammonium sulfite, thereby reducing the amount of evaporation required to crystallize the salts.

With high capacity buffer solutions where as much as 50% of the solution would be evaporated to produce steam for the stripper, dilution water should be added to the scrubber feed. This permits the stripper to operate with fewer stages. Such placement of dilution water would necessarily require the use of a condensate stripper. Dilution water should not be added to the stripper feed or at the top of the stripper because this would reduce the $SO_2$ vapor pressure of the solution and thereby increase the steam requirements.

If steam stripping is used in the presence of acid solids such as $K_2S_2O_5$, the dilution water should be added to the top of a countercurrent stripper where it will dissolve additional $K_2S_2O_5$ and thereby increase the $SO_2$ vapor pressure and reduce the steam requirements. Stripping steam would be provided by evaporation of bottoms solution from the stripper. The concentration/dilution effects should serve to reduce the net steam requirements. It is important that this stripping be carried out in a countercurrent stripper, because solution evaporation and crystallization of $K_2S_2O_5$ in the bottom stage will significantly reduce the $SO_2$ vapor pressure over that stage.

## HEAT RECOVERY

Almost all systems with steam regeneration include condensation of water from the product $SO_2$. Heat recovery from this condenser can result in substantial energy savings. At atmospheric pressure 90% of the $H_2O$ vapor can be condensed at 90-95°C. Possible methods of heat recovery include multiple-effect evaporators/strippers, vapor compression cycles, use or production of low pressure steam, and other methods of system integration.

Multiple-effect evaporation or stripping as in Figure 4 is particularly attractive. Condensation of $H_2O$ from the product of the first-effect, higher-pressure stripper is used to produce steam from the second-effect stripper, which operates at lower temperature and pressure. The number of effects is limited by the maximum temperature, usually 100°C to avoid sulfite disproportionation, and by the need to avoid excessively low pressure in the final effect. Practically, two or three effects should be feasible. The system steam requirements would essentially be inversely proportional to the number of effects. However, multiple effects necessarily increase the operating and design complexity of the system. The need for multiple parallel strippers can result in capital cost increases, but in the case of large systems, multiple strippers may be required to handle the full stripping load in any gas.

Steam generated during condensation of $H_2O$ from the product $SO_2$ could be utilized in a single effect if its pressure is increased by

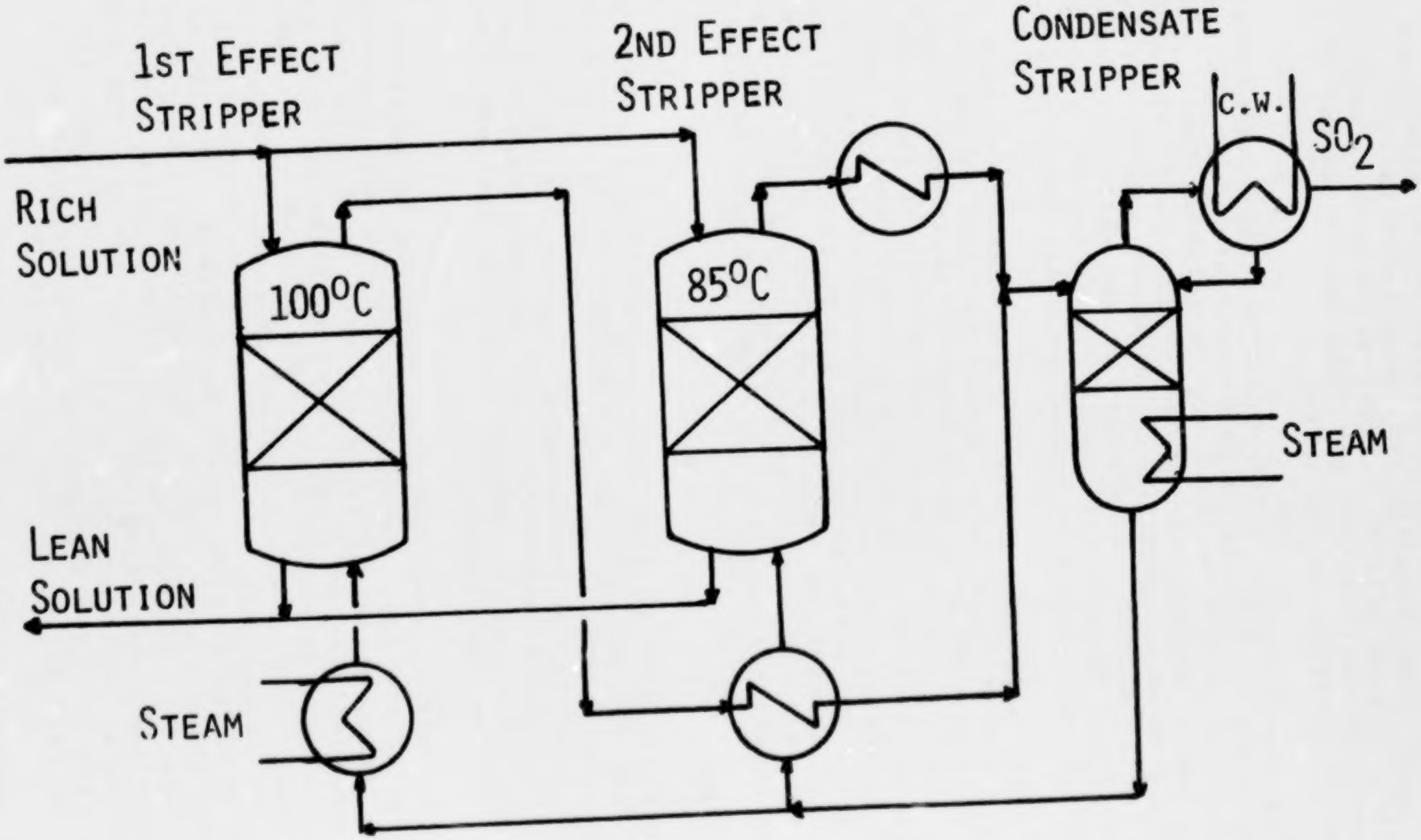

Figure 4. Double effect stripping

mechanical compression or by a steam ejector. Mechanical compression would permit the stripper to operate on a minimum amount of electric power, rather than relying on steam generated in the main boiler. Assuming that steam could be generated at 85°C/0.6 atm in the condenser, approximately 15 kwh of power would be required to recycle one million Btu's of steam. A steam ejector would permit compression to be accomplished at minimal capital cost without rotating equipment. About 0.4 lbs of steam at 600 psia would be required to provide 1.0 lbs of steam heat to a single-effect evaporator at 90°C with an allowance of 15°C for driving force and boiling point elevation.

Many steam regeneration systems can be effectively operated below atmospheric pressure at temperatures as low as 70-80°C. Under these conditions it is attractive to operate the stripper or evaporator with atmospheric or vacuum steam exhausted from a turbine. Thus the effective cost of energy for the steam stripping system can be substantially reduced. Integration with exhaust from a power turbine could be difficult because low pressure steam would have to be transported over a large distance. However it is sometimes attractive to use moderate-or high-pressure steam to drive fans and pumps in the flue gas desulfurization-system, and then to use exhaust steam from the turbine drivers in the stripping system.

Other miscellaneous methods of heat recovery could also be significant. Boiler feedwater could be preheated by condensing water from the $SO_2$ product. However, this would require extensive integration with the power production system. The $H_2O$ condenser could be used to preheat feed to the stripper, thereby eliminating the need for a cross-exchanger.

## SULFATE FORMATION AND REMOVAL

In most steam regeneration systems some sulfate is formed irreversibly by the oxidation and/or disproportionation of bisulfite. Unless intentionally removed by other means, dissolved sulfate will accumulate in the system to the point of uncontrolled crystallization of the sulfate salt. The accumulation of dissolved sulfate reduces the effective solubilities of other salts by the common ion effect. In systems where solubilities determine steam requirements, such as the Wellman-Lord process, sulfate accumulation will degrade system performance. Furthermore any sulfate formation ultimately results in a sulfate byproduct and usually requires alkali makeup. Therefore it is desirable to minimize sulfate formation and provide for effective sulfate removal.

As much as 5 to 10% of the $SO_2$ absorbed by a system such as the Wellman-Lord process may be oxidized to sulfate in the absorber. However, there is little information on the variables affecting bisulfite oxidation. The physical absorption and mass transfer of oxygen through the liquid phase is probably important. Therefore, oxidation rates should vary directly with oxygen concentration in the flue gas and should be greater in absorbers with larger amounts of mass transfer capability. It is also expected that flue gas impurities such as iron (from the flyash) and nitrogen oxides may act as catalysts for the oxidation (Graefe et al, 1970). There is some evidence that any $NO_2$ in the flue gas can react stoichiometrically with bisulfite to give sulfate and $N_2$ or $NH_4^+$ (Sawai and Gorai, 1977). Prescrubbing of the flue gas could remove flyash and possibly $NO_2$ and thereby reduce rates of oxidation in absorber. Prescrubbing could also remove HCl and $SO_3$ which would otherwise be absorbed and accumulate as dissolved chloride and sulfate. Oxidation inhibitors have been tried with limited success in the Wellman-Lord process (Pedroso, 1976).

Sulfate may also be formed by the disproportionation of bisulfite to thiosulfate ($S_2O_3^=$) and sulfate. The reaction probably proceeds as the formation of trithionate followed by hydrolysis (Battaglia and Miller, 1968; Foerster and Hornig, 1922):

$$2H^+ + 4HSO_3^- + S_2O_3^= \rightleftarrows 2S_3O_6^= + 3H_2O$$

$$2S_3O_6^= + 2H_2O \rightleftarrows 2SO_4^= + 2S_2O_3^= + 4H^+$$

---

$$4HSO_3^- \rightleftarrows 2SO_4^= + S_2O_3^= + 2H^+ + H_2O$$

The rate expression for trithionate formation is given by:

$$\frac{d[HSO_3^-]}{dt} = -k[H^+]^3[S_2O_3^=]^3[HSO_3^-]$$

$$k = 2.2 \cdot 10^6 \underline{M}^{-6}\ \text{sec}^{-1}\ \text{at}\ 70^\circ C$$

(Battaglia and Miller, 1968)

Since the net disproportionation produces thiosulfate, which also shows up in the rate expression, the reaction is autocatalytic. As more thiosulfate accumulates the disproportionation occurs even faster. Low pH also appears to give faster rates of disproportionation. Significant disproportionation has been observed in the Wellman-Lord Process (Bailey, 1974) and the $NH_3$-based steam-stripping process when regeneration is carried out at temperature greater than 100°C. Disproportionation has been essentially eliminated in the Wellman-Lord process by operating a vacuum evaporator at 90-100°C with a liquid purge to minimize thiosulfate accumulation. When using an aluminum sulfate scrubbing solution, I.C.I. avoided disproportionation by boiling a portion of the liquor with copper sulfate in the presence of $SO_2$ to eliminate thiosulfate from the system (Applebey, 1937). Potentially, disproportionation could be reduced by minimizing solution holdup in the stripper and evaporator. Thus the stripper should use low-holdup packing rather than trays and solution contained in the evaporator should either be pure water or scrubbing solution containing no dissolved $SO_2$.

Oxidation and disproportionation may be substantially reduced in systems using aldehydes such as glyoxalic acid. These systems normally operate at very low pH conditions where there is no dissolved bisulfite and very little dissolved $SO_2$. All of the $SO_2$ is absorbed as the hydroxy-sulfonate complex. Therefore, rates of oxidation and disproportionation of the dissolved $SO_2$ species should be greatly inhibited.

Sulfate can be removed from steam regeneration systems by solution purge or by the controlled crystallization of salts such as Glauber's salt ($NaSO_4 \cdot 10H_2O$) or gypsum ($CaSO_4 \cdot 2H_2O$). Direct solution purge is attractive only for systems with inexpensive absorbents consisting primarily of dissolved sulfate, such as aluminum sulfate. Absorbent systems that use sodium alkali, such as sodium citrate or sodium sulfite/bisulfite, can selectively remove sulfate by the refrigerated crystallization of Glauber's salt. Buffered systems can usually crystallize gypsum from stripped solution by adding lime or limestone (Applebey, 1937). Crystallization of gypsum from alkali sulfite/bisulfite systems usually requires complicated processing with the addition of both lime and $SO_2$ (Johnstone and Singh, 1940).

## MORPHOLOGICAL PROCESS ALTERNATIVES

A number of evolutionary alternatives have been generated for reducing steam consumption and handling sulfate, as discussed in the preceding sections. Many of these innovations can be used simultaneously, so a large number of combinations are possible. Table 2 represents independent groups of alternatives. A complete process can be defined by selecting one alternative from each group. The alternative groups are distinguished as being reactant alternatives or flowsheet alternatives.

### Reactant Alternatives

In general the scrubbing solution must use at least one alkali and may or may not use an acid buffer, except in systems which use only aldehydes. The alkali additives are divided into three groups. The strong alkalis - $Na^+$, $K^+$, $Mg^{++}$ - are usually the least expensive and are nonvolatile. $Na^+$ has been the dominant alkali selected in development work, but $K^+$ and $Mg^{++}$ have unique solubility characteristics which could make them more or less attractive. The weak alkalis - $NH_4^+$, methylamine, ethanolamine - act as buffers at pH 8-10 and are therefore suitable for sulfate removal as $CaSO_4$. They also generally have large solubilities. However, $NH_3$ has problems with volatility in the scrubber and other amines tend to be quite expensive. The buffering alkalis - $Al^{+3}$, ethylenediamine - potentially reduce steam requirements by straightening the equilibrium cruve and by increasing the temperature coefficient of $SO_2$ vapor pressure.

The acid buffer alternatives include the use of no acid additive or the use of several possible acids with significant buffer capacities in the pH range 4.5-6.0. With no acid additive, the buffer system must be sulfite/bisulfite or a buffering base. Thus, only sulfite or pyrosulfite salts are likely to crystallize in the case of solution evaporation. The use of buffering acids straightens the equilibrium curve and adds a degree of freedom to the solids that can be present in saturated solution. The buffers would also permit effective use of gypsum crystallization for sulfate removal. Lower pH buffers such as glycolate ($pK_a$=3.85) are probably not attractive because of low solution capacity for $SO_2$ at the low pH.

Table 2: MORPHOLOGICAL ALTERNATIVES

Reactants

1. Alkali -- (a) strong - $Na^+$, $K^+$, $Mg^+$
   (b) weak - $NH_4^+$, methylamine, ethanolamine
   (c) buffering-ethylenediamine, $Al^{+3}$
2. Acid -- (a) none
   (b) high $pK_a$ - phosphoric, adipic, citric, phthalic, sulfosuccinic
3. Aldehyde-- glyoxalic acid, glyoxal

Flowsheets

4. Evaporation/dilution -- none, stripper bottoms/scrubber feed, stripper bottoms/stripper feed
5. Number of scrubber feeds -- one, two
6. Additional phases -- none, one, two
7. Heat recovery -- single-effect, multiple-effect, vapor compression, low-pressure steam
8. Sulfate removal -- purge, Glauber's salt, gypsum, other sulfate

Aldehyde reactants - glyoxalic acid, glyoxal - are unique in requiring no alkali additives. They should generally result in excellent steam requirements, but may have to be used with lower gas temperatures, resulting in high costs for flue gas cooling.

## Flowsheet Alternatives

There are five important groups of flowsheet alternatives. These can interact quite strongly with the selection of reactants and/or the selection of other specific flowsheet alternatives.

If solution evaporation is used for steam generation, the resulting dilution water should not be added to the stripper feed unless pyrosulfite or buffer acid solids are present. Avoiding solution evaporation can be advantageous to the extent that it avoids corrosion-resistant materials in the evaporator and eliminates boiling point elevation (important with some methods of heat recovery).

A dual scrubber feed eliminates the detrimental effect of nonlinear equilibria. Since buffers accomplish the same purpose, the combination of buffer additives with a dual scrubber feed is not attractive.

A scrubber system can be operated with additional solid or liquid phases with or without solution evaporation. The effect of an additional phase interacts with reactant selection and the mode of evaporation/dilution.

Heat recovery options can usually be incorporated with any reactant or flowsheet combination. However, multiple-effect evaporation or low-pressure steam would be less attractive with systems using temperature effects to reduce steam requirements, since portions of the regeneration would occur at lower temperature.

The optimum method of sulfate removal interacts strongly with the reactant selection. It may also vary depending on the mode of evaporation/dilution.

## CONCLUSIONS

1. It will be difficult to develop a steam regeneration system which is superior to the Wellman-Lord process in steam requirements and simplicity, though there are many possibilities.

2. Without gas cooling or solids crystallization, ethylenediamine sulfate or chloride solution may be effectively used with lower steam requirements than Wellman-Lord.

3. A properly designed system based on the crystallization/dissolution of $K_2S_2O_5$ solids should give steam requirements competitive with Wellman-Lord.

4. Aluminum salt solution could be a competitive scrubbing solution when used in combination with gas cooling.

5. Nonvolatile aldehydes have a definite potential for reduced steam requirements, although they may also require non-adiabatic flue gas cooling.

6. The use of evaporation and/or crystallization generates a number of possible alternatives that have not been fully explored.

## ACKNOWLEDGEMENTS

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# APPLICATION OF DRY SORBENT INJECTION FOR $SO_2$ AND PARTICULATE REMOVAL

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## ABSTRACT

Integrated processes designed to remove two or more pollutants simultaneously from a coal-fired boiler flue gas are of considerable interest from both an economic and operational standpoint. One such approach is through the injection of dry sorbent in the flue gas duct followed by collection of spent material and fly ash in the electrostatic precipitator or baghouse.

A review of literature indicates that most of the work conducted to date is confidential and concentrated in specific areas for sales purposes without due consideration to understanding the basic parameters involved in the process. Previous investigations have confirmed that alkaline material containing calcium and magnesium are relatively ineffective in removing $SO_2$, while the alkaline materials containing sodium have been identified as attractive dry sorbents. A higher flue gas temperature generally results in better $SO_2$ removal, but basic information concerning kinetics and thermodynamics of the heterogeneous reaction is lacking. It has been concluded that a systematic study of the process under well-characterized and controlled conditions simulating practical utility boiler applications is necessary before the technology can be considered for constructing commercial installations.

EPRI's current efforts in dry $SO_2$ removal research are focused on bench-scale research to provide a data base that will define the range of operating parameters for future pilot- and full-scale installations. The effects of sorbent type, residence time, temperature, particle size, and stoichiometric ratio on $SO_2$ removal efficiency and sorbent utilization will be evaluated.

Future plans include formulation of a complete program at a larger scale based on the data obtained from the bench-scale study. Additional future work will concentrate on the problem concerning the effect of sorbent injection on air preheaters, waste disposal of the spent material, availability and supply of various sodium based sorbents, and an economic evaluation.

# APPLICATION OF DRY SORBENT INJECTION FOR $SO_2$ AND PARTICULATE REMOVAL

## INTRODUCTION

To comply with the emission standards promulgated by EPA for coal-fired boilers, a considerable effort towards the development of sulfur oxide removal equipment has been mounted. To date, efforts have focused on wet lime/limestone scrubbing of Eastern high-sulfur coals. However, interest in developing a practical and low cost $SO_2$ removal system for Western low sulfur coal has increased significantly in recent months due to pressures from local regulatory bodies and passage of the 1977 Clean Air Act Amendments. Dry sorption of $SO_2$ is a relatively new technology but indicates promise of becoming a commercially viable process.

Dry $SO_2$ removal possess features which show promise for lower overall capital/operating costs and greater reliability compared to wet scrubbing. The advantages of dry scrubbing are:

- Lower capital cost since particulate and $SO_2$ removal can be achieved in a single device.
- Anticipate greater reliability and lower maintenance due to the simplicity of the process.
- 3-5% energy savings compared to wet scrubbers.
- Savings of 1 GPM/MW wet scrubber water consumption.

While the process sounds attractive, it does have some disadvantages:

- Moderate $SO_2$ removal efficiency (60-70%).
- High reagent cost
- Problems in connection with availability, supply and transportation of the sorbents.
- Lack of operating experience.
- Spent sorbent disposal requirements unknown/lack of commercially available regeneration process.

It appears from the above analysis that dry scrubbing shows promise for the western part of the country where only moderate $SO_2$ removal is needed and reagents are generally available.

## LITERATURE SURVEY

EPRI's report No. FP-207(3) "Evaluation of Dry Alkalis for Removing Sulfur Dioxide from Boiler Flue Gases" summarized the various known aspects of dry scrubbing processes. From the review of this report, it appears that most of the development work(1,2,6,7,8,9,11) conducted to date is oriented towards sales promotion without due consideration to providing specific design criteria relative to the process. Basic technical information pertaining to energy consumption, resource requirements, capital and operating costs is lacking.

Tests conducted by Air Preheater Co.,(5) at the Public Service of New Jersey's Mercer station are probably the best to date in terms of identifying and quantifying the effect of the major controllable variables in the process. These tests (see Table 1) and work conducted by others(3,13) have shown significantly higher reactivity of alkaline material containing sodium compared to calcium and magnesium. For this reason, future work is expected to be concentrated in investigating various sodium based dry alkaline materials.

Temperature and stoichiometric ratio were identified in the Mercer study(5) as important process variables. Table 1(5) shows that $SO_2$ removal efficiency increases as the temperature and stoichiometric ratio are increased. However, no attempt was made to explain these results in terms of rate controlling steps for the heterogeneous reaction. Since both duct and baghouse were operated at high temperatures, extrapolation of the data presented in Table 1 to full scale where collection occurs at low temperature, is questionable. Data presented in Table 1 for sorbent utilization should be used with caution because of the questionable validity of the assumptions(5) made.

Table 1

Results from Mercer Tests

| | Stoich. Ratio = 1 | | | Stoich. Ratio = 3 | | |
|---|---|---|---|---|---|---|
| Additive | Conv. Eff.* % | Util. Eff.* % | Conv. In Gas* % | Conv. Eff. % | Util. Eff. % | Conv. in Gas % |
| Sodium Bicarbonate-270°F | 32 | 32 | -- | 48 | 16 | 12 |
| Sodium Bicarbonate-350°F | 48 | 48 | 26 | 76 | 26 | 12 |
| Sodium Bicarbonate-600°F | 90 | 90 | 72 | -- | -- | -- |
| Nahcolite -350°F | 65 | 65 | 11 | 85 | 30 | 24 |
| Nahcolite -600°F | 94 | 94 | 60 | -- | -- | -- |
| Hydrated Dolomite Lime -350°F | -- | -- | -- | 20 | 7 | 75 |
| Hydrated Dolomite Lime -600°F | 20 | 20 | 95 | 38 | 13 | 80 |

*Nomenclatures:
Conv. Eff. = $SO_2$ Conversion Efficiency
Util. Eff. = Additive Utilization Effectiveness
Conv. in Gas = $SO_2$ Conversion in the gas stream or in suspension.

Tests by Wheelabrator-Frye Inc.(3) at the Nucla Station of Colorado Ute Electric Association showed $SO_2$ removal efficiency in the range of 50 to 70%. Since these tests were conducted on a confidential basis, details of the tests -- such as particle size, temperature-time history -- are not readily available.

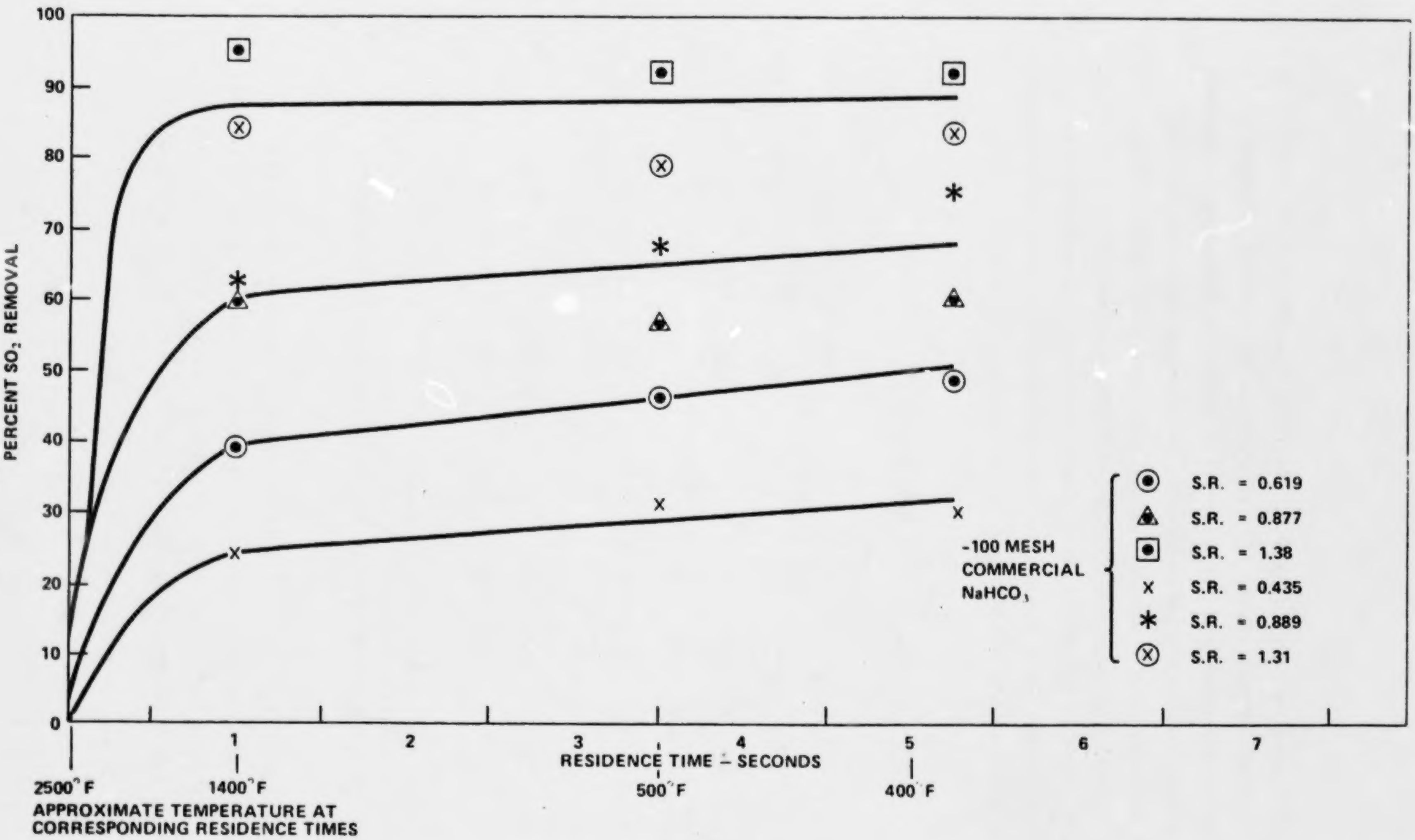

FIGURE 1

EFFECT OF RESIDENCE TIME AND TEMPERATURE ON $SO_2$ REMOVAL AT VARIOUS STOICHIOMETRIC RATIOS

$SO_2$ GAS INJECTED INTO BURNER SECONDARY AIR FROM THE SUPERIOR OIL COMPANY

The results of tests conducted by The Superior Oil Co.(3) in conection with Nahcolite injection in a flue gas duct are presented in Figure 1. It is evident from this figure that as residence time, temperature and stoichiometric ratio are increased, $SO_2$ removal efficiency also increases. The effect of temperature is more pronounced between the temperature range 1400°F to 2500°F. Residence time above 1 second does not result in an appreciable increase in $SO_2$ removal efficiency. It should be noted that these data were obtained on flue gas from an oil-fired furnace with synthetic $SO_2$ gas injection and hence might not be applicable to flue gas from a coal-fired boiler.

Figure 2 shows the comparison of various sodium alkalis tested by Superior.(3) Results clearly show the superior reactivity of biocarbonate containing compounds compared to carbonates. The higher reactivity of bicarbonate may be due to the porous structure of the material caused by the decomposition reaction:

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

The formation of $CO_2$ and $H_2O$ leaves a porous $Na_2CO_3$ which allows easier passage of $SO_2$ resulting in an improved rate of diffusion of $SO_2$. The final reaction between $Na_2CO_3$ and $SO_2$ is assumed to take place as follows:

$$Na_2CO_3 + SO_2 + 1/2\ O_2 \rightarrow Na_2SO_4 + CO_2$$

It is evident from the above reactions that the kinetics involved in the dry scrubbing process are much more complex.

Recently, tests were conducted by Wheelabrator-Frye Inc.(14) at Stanton Station of Basin Electric to investigate the use of fabric filter for fly ash and $SO_2$ removal by nahcolite injection. Unfortunately, no information concerning the results from these proprietary tests is available at present.

In summary, the presently available data on the dry sorbents are encouraging, but there is a need to obtain more data to better characterize and optimize the removal process in terms of the pertinent parameters.

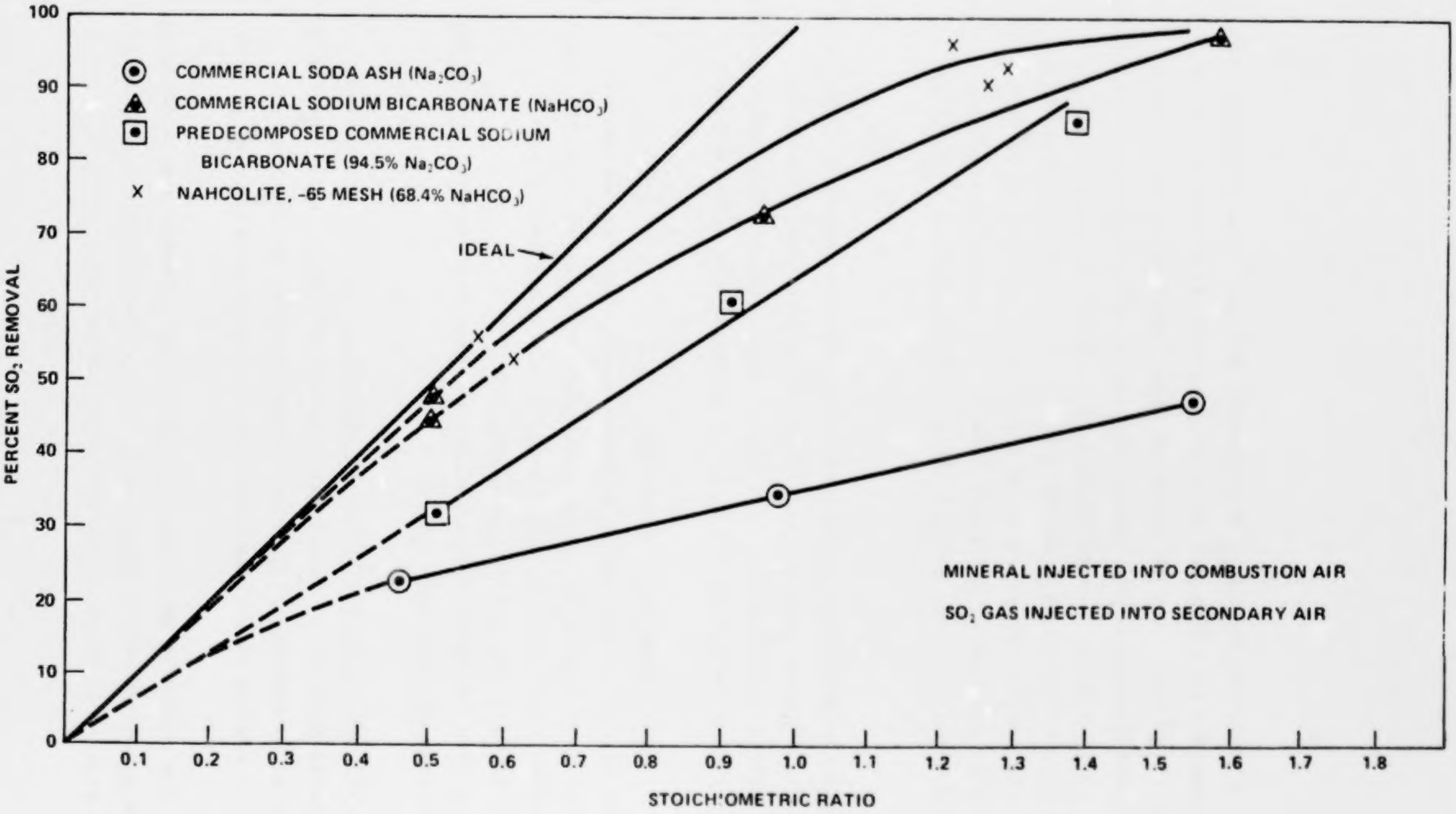

FIGURE 2

EFFECT OF INJECTING VARIOUS SODIUM
MINERALS ON PERCENT $SO_2$ REMOVAL
FROM THE SUPERIOR OIL COMPANY

## EPRI'S ACTIVITIES

Before going into the details of EPRI's plan in the dry scrubbing area, it is necessary to examine various methods proposed to remove $SO_2$ with solid alkaline materials.

These methods are:

- Addition to fuel
- Injecting the agent into the furnace separate from the fuel
- Contacting the gas containing $SO_2$ with a fixed or fluidized bed of sorbent
- Injecting the agent in the flue gas duct followed by collection in an electrostatic precipitator or baghouse

One of the serious drawbacks of adding the agent to fuel or combustion zone injection is that it could interfere with the operation of the boiler. Problems associated with high pressure drop, mechanical complexity, cost and ash handling are yet to be solved before the fixed and fluidized bed processes could become commercial. Accordingly, it seems that the only practical dry process application in the near future is through injection of sorbent in the flue gas duct followed by collection in an electrostatic precipitator or fabric filter. However, before, this technology can be applied to a commercial installation, a systematic study quantifying the effects of controllable parameters and examining application related problems, is necessary.

For this reason, EPRI's current efforts are focused on a bench-scale research designed to quantify the effect of various significant parameters on $SO_2$ removal efficiency and sorbent utilization. The bench-scale study will be conducted at a scale of 725 SCFM under well characterized and controlled conditions simulating a utilty boiler application. The program (see Table 2) is designed to obtain data pertaining to the effect of residence time, temperature, particle size, stoichiometric ratio, sorbent type on $SO_2$ removal efficiency and sorbent utilization. Electrical resistivity of the spent material will be determined to investigate the feasibility of using dry scrubbing process to enhance particulate collection in electrostatic precipitators. The effect of sorbent injection on $NO_x$ and particulate emissions will also be evaluated. The data relating to the degree of reaction occurring in suspension versus on the filter cake of the bags or precipitator plates will also be gathered. Assuming successful completion of the bench-scale research, future work will be aimed at pilot and full-scale demonstrations.

Table 2

Test Program for EPRI's Bench-Scale Study

| No. | Variable | Range |
|---|---|---|
| 1. | Duct temperature | 300, 450, 600, 800, and 1100°F |
| 2. | Stoichiometric ratio | 0, 1, 2 |
| 3. | Residence time in the duct | 0, 1, 2, and 4 sec. |
| 4. | Type of sorbent | Nahcolite*, $NaHCo_3$*, $Na_2CO_3$, trona* |
| 5. | Sorbent particle size | -10 mesh, -65 mesh, -100 mesh and -200 mesh |

*Including calcined form.

WASTE DISPOSAL/REGENERATION

No study on dry $SO_2$ removal would be complete without evaluating the disposal aspects of spent sodium sorbents. A number of investigators(1,2) have proposed several chemical and mechanical fixation methods for disposal of spent sorbent based on theoretical considerations. To present a clear picture to utility industries, a detailed economic analysis of various options is necessary. EPRI's future plans will be concentrated in examining and screening these options for utility application.

Another alternative to waste disposal is the regeneration(7,15) of feed sorbent material from spent sodium compounds. This would obviate the problem in connection with availability and supply of various sodium containing compounds. To present an overall picture, the regeneration process will have to be integrated with dry scrubbing. A description of sodium regeneration processes as applied to dry scrubbing is presented by Dalton.(15)

## SUMMARY

Dry scrubbing appears to be an attractive alternative in some cases, but further research is needed before the technology can be considered for commercial application. Sodium based sorbents have been identified as superior reactants in dry state compared to sorbents containing calcium and magnesium. The bench-scale study sponsored by EPRI will provide answers to questions related to the effect of controllable parameters involved in the dry scrubbing processes. It is anticipated that follow-on efforts will include construction and operation of a pilot plant, and subsequently, a full-scale plant. The problem of disposal of waste sodium sorbents must be solved before the technology can be further considered for commercial application.

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# UNPRESENTED PAPERS

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# OPERATING EXPERIENCES WITH KAWASAKI MAGNESIUM-GYPSUM FLUE GAS DESULFURIZATION PROCESS

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## ABSTRACT

Construction of the first and the second commercial plants using a Magnesium Gypsum Flue Gas Desulfurization Process recently developed by KAWASAKI HEAVY INDUSTRIES, LTD. (KHI) were completed and the trial runs were finished in the beginning of 1976. An outline of the processing equipment, and performance data in the trial runs of the flue gas desulfurization plant for Japan Exlan Co., one of these commercial plants, are summarized in this paper.

Construction of the Japan Exlan plant was completed in the end of 1975, and it has remained in operation, after a 2-month trial run, since March 1976. In this plant, lime is used as the absorbent agent (with addition of small amounts of magnesium hydroxide) and gypsum is recovered as a byproduct from the plant. A mixed slurry of calcium and magnesium solids is used in the absorber, in which sulfur dioxide removal efficiency is more than 93 percent. Stable continuous operation, with no trouble of scaling, has been maintained since the trial run.

We have found a possibility to refine this process to a high degree, improving on the present Magnesium-Gypsum Process, based on our experiences obtained in the runs at the above commercial plants and on the results of several investigations of our own related to the process.

The results of the above investigations and an outline of the improved process are also summarized in this paper.

# OPERATING EXPERIENCES WITH
# KAWASAKI MAGNESIUM-GYPSUM FLUE GAS DESULFURIZATION PROCESS

## INTRODUCTION

KHI constructed two commercial plants of the newly developed Magnesium Gypsum Flue Gas Desulfurization Process at the end of 1975, which have been in stable operation after the trial run since the beginning of 1976.

The KHI Magnesium-Gypsum Flue Gas Desulfurization Process was developed and brought into practical use based on our own experimental study on a pilot plant in 1972 and 1973 with a magnesium absorbent in which we at KHI have a rich experience.

We obtained an order of the first commercial plant by this process from Unitika Co., Okazaki Works, and that of the second one from Japan Exlan Co., Saidaiji Works, 1974, and both of these plants were constructed in 1975.

This process is suitable for the flue gas of coal firing as well as that of oil firing, and is expected to be a main process of KHI's flue gas desulfurization plant in the future.

Lime is used in the plant for Japan Exlan Co., as in the case of our pilot plant, meanwhile, limestone is used as a main absorbent agent with a little addition of lime in the plant for Unitika Co. Gypsum is recovered as a by-product in the both plants. Results of the trial run and successive commercial run of the flue gas desulfurization plant for Japan Exlan Co. and our several investigations related to this process, improvements of the process according to the above results and an outline of a proposal of the flue gas desulfurization plant applying the improved process are summarized in this paper.

# I. RESULTS OF RUN OF THE FLUE GAS DESULFURIZATION PLANT FOR JAPAN EXLAN CO.

The flue gas desulfurization process adopted to Japan Exlan plant is a standard Magensium-Gypsum Process, in which lime is used as an absorbent and gypsum is recovered as a by-product.

This plant was ordered in August 1974, constructed in December 1975, and has been in commercial run since March 1976 (after the two-month trial run beginning in January 1976).

## A. OUTLINE OF EQUIPMENT

### 1. Design Specification

The absorption section is divided into two units for the convenience of operation, but the other sections such as oxidation, gypsum separation, raw material feeding and magnesium hydroxide regeneration are each common units which serve the two absorption units.

Location : Japan Exlan Co., Saidaiji Works, Japan

Use : Desulfurization of the flue gas from the boilers for power generation and for supply of process steam

Fuel of boiler : S, 2 — 3 wt%, Bunker C Oil

Gas flow rate : No.1 Absorber : 160,000 Nm$^3$/h
No.2 Absorber : 140,000 Nm$^3$/h

SOx concentration (dry) : Absorber Inlet : 1,412 ppm
: Absorber Outlet : 90 ppm

Particulates concentration (dry) : Absorber Inlet : less than 0.2 g/Nm$^3$
: Absorber Outlet : less than 0.1 g/Nm$^3$ (after reheating)

Absorbent agent : $Ca(OH)_2$ : 953 kg/h
$Mg(OH)_2$ : 6 kg/h

By-product : Gypsum : 2,214 kg/h
(not including the moisture)

Exhanust gas heating system : Afterburner

The general view and the general arrangement of this plant are shown in Figures 1 and 2, respectively.

The specifications of the main equipment are shown in Table 1.

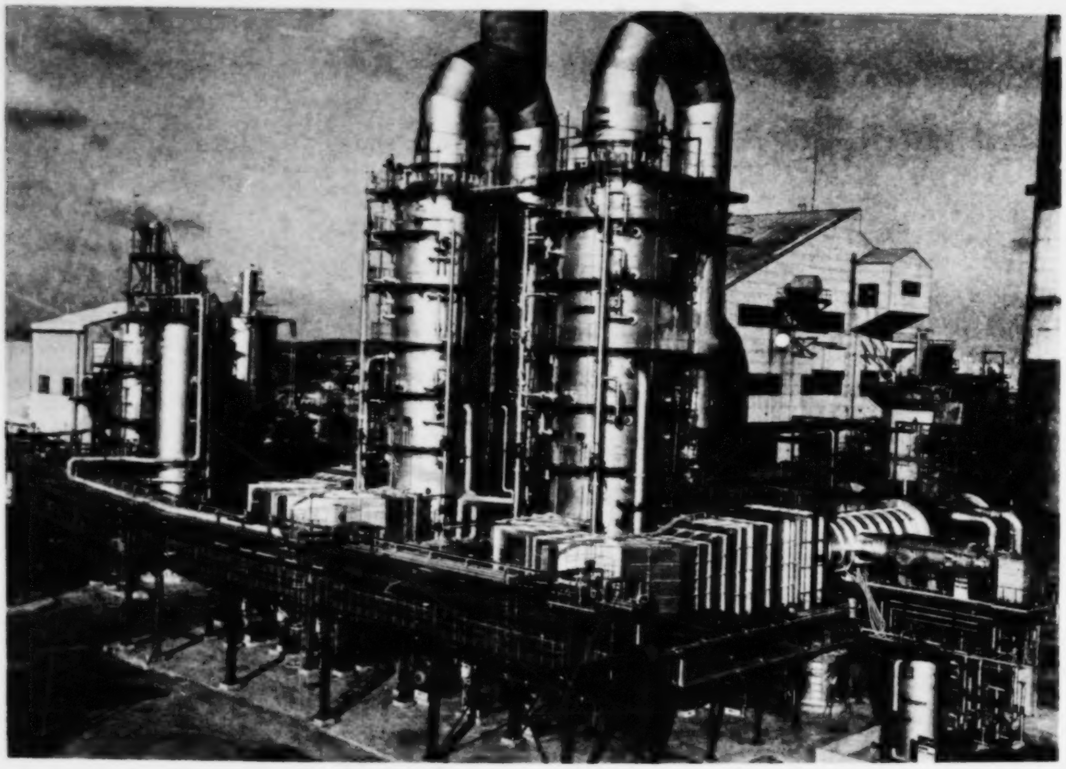


Figure 1. General View of the FGD Plant for Japan Exlan Co.

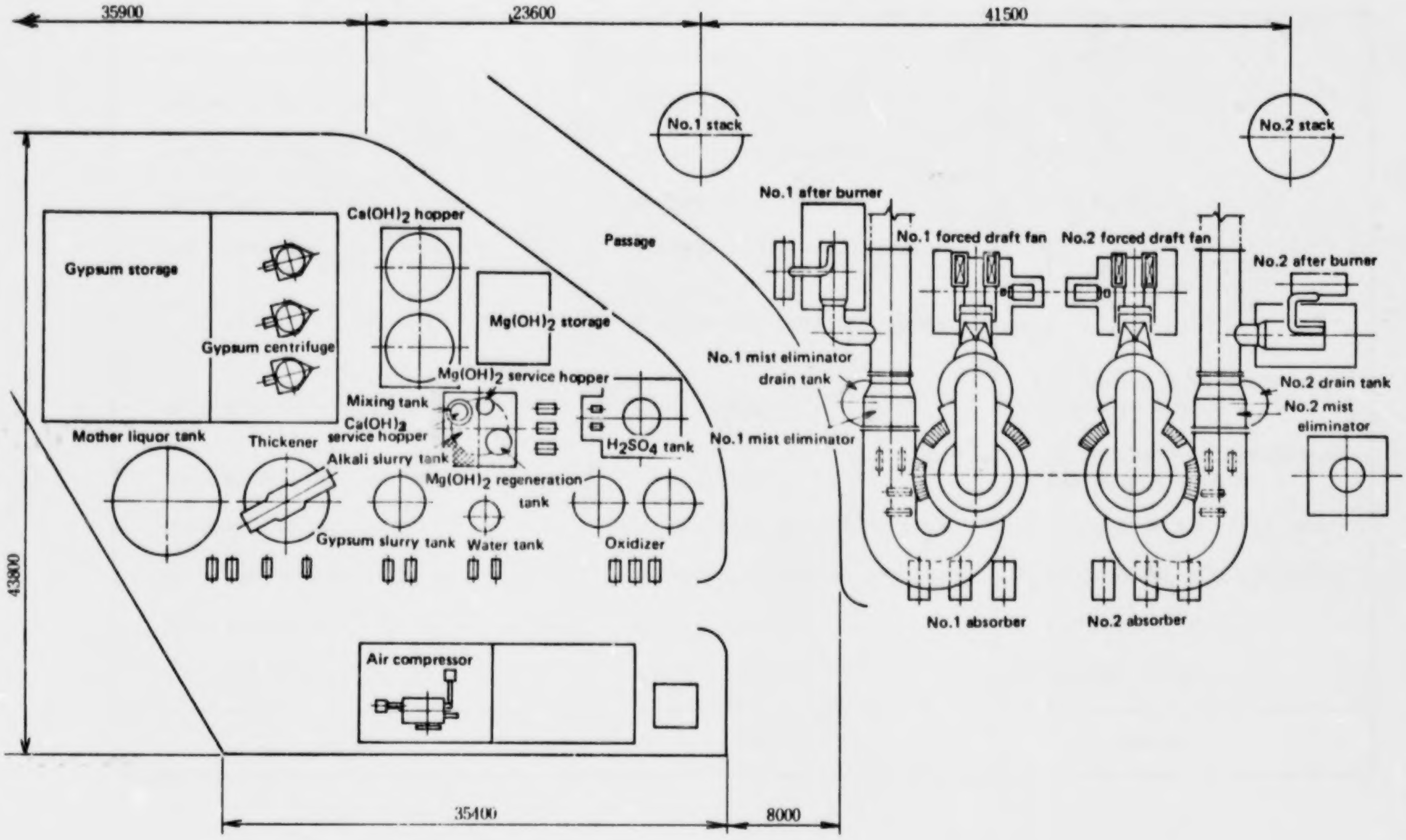


Figure 2 General Arrangement of the FGD Plant for Japan Exlan Co.

## Table 1. MAIN EQUIPMENT

| Item | Type | Capacity |
|---|---|---|
| No.1 Absorber | Multi - Venturi | 160,000 $Nm^3/h$ |
| No.2 Absorber | Multi - Venturi | 140,000 $Nm^3/h$ |
| No.1 Forced draft fan | Turbo, with double suction | 160,000 $Nm^3/h$ x 350 mmAq |
| No.2 Forced draft fan | Turbo, with double suction | 140,000 $Nm^3/h$ x 350 mmAq |
| No.1 Absorbent circulation pump | Centrifugal | 530 $m^3/h$ x 55 m x 3<br>(2 out of 3 in operation) |
| No.2 Absorbent circulation pump | Centrifugal | 530 $m^3/m$ x 55 m x 3<br>(2 out of 3 in operation) |
| No.1<br>No.2 Oxidizer | Cylindrical bubbling tower with air | |
| Air compressor for oxidizer | 2-stage turbo compressor | |
| Regeneration tank | Cylindrical vertical | 3.3 $m^3$ |
| Alkali slurry tank | Cylindrical vertical | 58 $m^3$ |
| Mother liquor tank | Cylindrical vertical | 180 $m^3$ |
| Sulfuric acid tank | Cone roof | 12 $m^3$ |

## 2. Description of the Process

The process flow diagram is shown in Figure 3.

The process consists of the following three sections;

a. Raw material feeding and magnesium hydroxide regeneration section.

b. Absorption section.

c. Oxidation and gypsum separation section.

a. Raw Material Feeding and Magnesium Hydroxide Regeneration Section:

Raw materials of lime and magnesium hydroxide are supplied from the hoppers to a mixing tank, in which they are mixed with water to form a slurry and are sent into a magnesium hydroxide regeneration tank.

In the regeneration, tank, mother liquor (solution of $MgSO_4$) which is circulating in the system and has no ability of absorbing the sulfurdioxide gas is regenerated as an absorbent, changing into $Mg(OH)_2$ by the reaction (1).

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4 \text{ ......... (1)}$$

The slurry of raw materials which contains lime and magnesium hydroxide is supplied to the absorber, after being stored in a alkali slurry tank.

b. Absorption Section: Flue gas from the boilers is sent to the absorber through a fan, is quenched by cooling water in the absorber, and then is contacted efficiently with a slurry of magnesium and calcium solids.

The $SO_2$ is absorbed and removed according to the reactions (2) and (3).

$$MgSO_3 + SO_2 + H_2O \rightarrow Mg(HSO_3)_2 \text{ ..............(2)}$$

$$CaSO_3 + SO_2 + H_2O \rightarrow Ca(HSO_3)_2 \text{ ..............(3)}$$

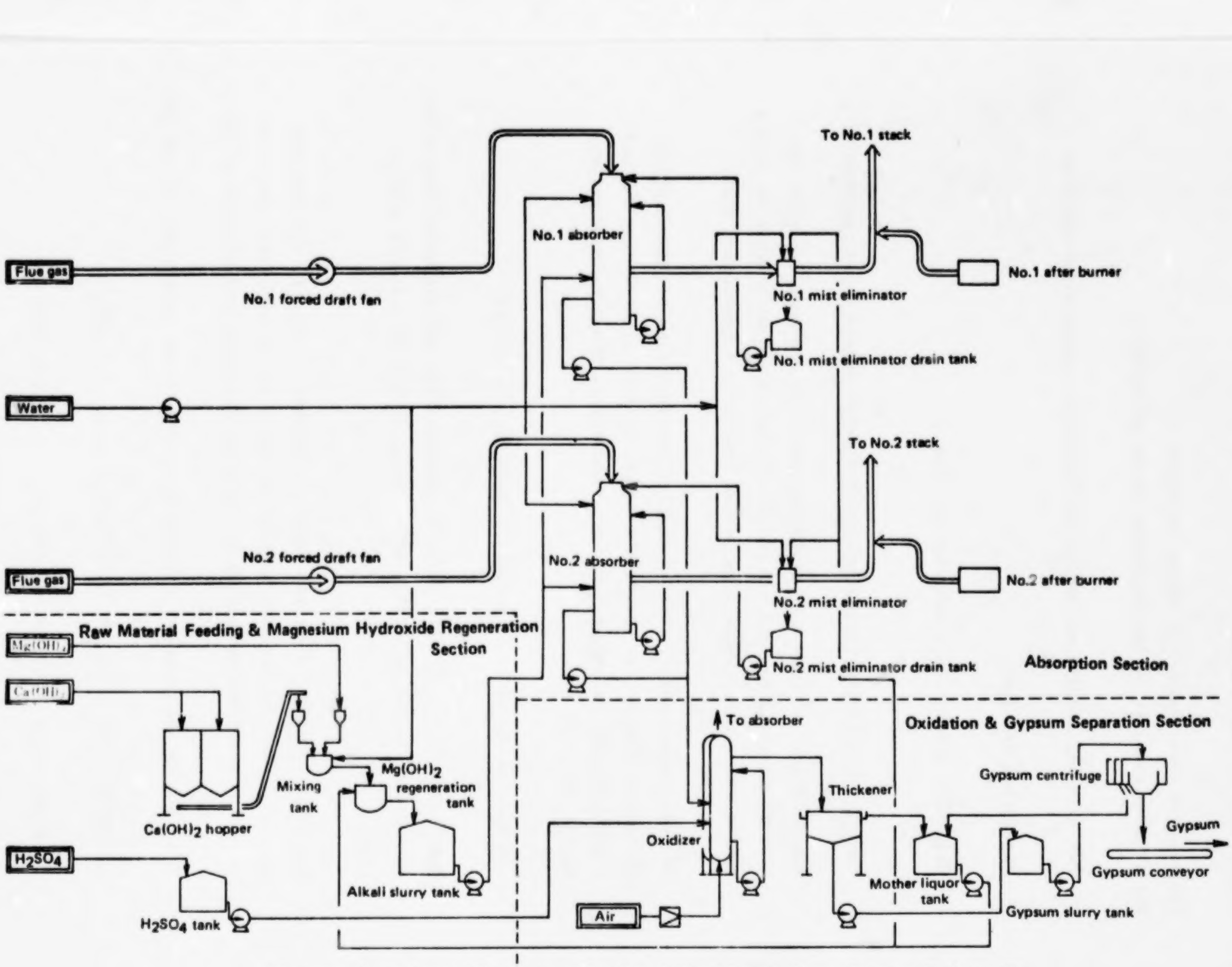


Figure 3 Flow diagrem of the FGD Plant for Japan Exlan Co.

After the elimination of mist and being reheated to prevent a steam plume, the clean gas is emitted to atmosphere.

Meanwhile, part of absorbent slurry is pumped to the oxidation and gypsum separation section ; the remainder is neutralized by the reactions (4) — (7).

$$Mg(HSO_3)_2 + Mg(OH)_2 \rightarrow 2MgSO_3 + 2H_2O \quad \text{............... (4)}$$

$$Mg(HSO_3)_2 + Ca(OH)_2 \rightarrow MgSO_3 + CaSO_3 + 2H_2O \quad \text{........ (5)}$$

$$Ca(HSO_3)_2 + Ca(OH)_2 \rightarrow 2CaSO_3 + 2H_2O \quad \text{............... (6)}$$

$$Ca(HSO_3)_2 + Mg(OH)_2 \rightarrow CaSO_3 + MgSO_3 + 2H_2O \quad \text{........ (7)}$$

Then, the neutralized slurry is circulated to the absorber to be re-used.

c. Oxidation and Gypsum Separation Section: The absorbent liquor which has been consumed to absorb $SO_2$, is supplied to an oxidizer from the absorption section and oxidized by air according to the reactions (8) ∿ (11). Consequently it becomes possible to separate magnesium from calcium, as the solid phase consists of only $CaSO_4$ and liquid phase consits of only $MgSO_4$.

$$CaSO_3 + \frac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4 . 2H_2O \quad \text{...............(8)}$$

$$Ca(HSO_3)_2 + \frac{-1}{2}O_2 + H_2O \rightarrow CaSO_4 . 2H_2O + SO_2 \quad \text{........(9)}$$

$$MgSO_3 + \frac{1}{2}O_2 \rightarrow MgSO_4 \quad \text{...............................(10)}$$

$$Mg(HSO_3)_2 + \frac{1}{2}O_2 \rightarrow MgSO_4 + H_2O + SO_2 \quad \text{...............(11)}$$

Alkali remaining in the slurry are neutralized through the reactions(12) and (13).

$$Ca(OH)_2 + SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow CaSO_4 . 2H_2O \quad \text{.........(12)}$$

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4 . 2H_2O + CO_2 \quad \text{...(13)}$$

At first we planned to supply $H_2SO_4$ in order to neutralize the excess of $Ca(OH)_2$, but $H_2SO_4$ is not used at present as it proved to be unnecessary.

Gypsum slurry from the oxidizer is dewatered by a thickener to a favourable concentration for a centrifuge (about 15%), and, separated into gypsum and mother liquor through a centrifuge.

The gypsum is taken out from the system as a by-product, and the rest liquor is pumped to the $Mg(OH)_2$ regeneration section and is re-cycled as absorbent.

The quantity of make-up of magnesium hydroxide is equal to the loss of magnesium(as $MgSO_4$)contained in the moisture of gypsum, and it is only a very small quantity.

## B. RESULTS OF TRIAL RUN

### 1. Progress and Outlook of Trial Run

Progress of the trial run is shown in Table 2.
The trial run was started in December 1975 and was completed in the middle of March 1976 with no major trouble.
We delivered the plant to the client after the trial run, and the plant passed an official test with no problem at the end of March 1976.

After an adjustment run (a test run in which an absorbent liquor is adjusted to be a designed condition), we had a minimum load run (15 – 20%) in the No.1 absorber and a maximum load run (100%) in the No.2 absorber, respectively, in which we could confirm the high efficiency with no problem.

In addition to the above, we confirmed the effects of such factors as pH of absorbent liquor, liquid-to-gas ratio, etc., on the absorption efficiency.

Table 2. PROGRESS OF TRIAL RUN PRACTISED

| Item \ Month | | 1975<br>Dec. | 1976<br>Jan. | 1976<br>Feb. | 1976<br>Mar. |
|---|---|---|---|---|---|
| Test run of each equipment, Run with water | | ├──────┤ | ├┤ | | |
| Adjustment run | | | ├────┤ | | |
| Maximum load run | | | | ├─┤ | |
| Several test run | | | | ├───┤ | ├──┤ |
| Gas load factor (%) | No.1 | | 15∿20 ├─┤ | 15∿20 ├──┤ 15∿35 ├───┤ | 10∿20 ├──┤ |
| | No.2 | | 80 ∿ 90 ├────── | ──┤ 95∿100 ├───┤ 60∿100 ├───┤ | 75∿100 ├──┤ |
| Sulfur in fuel (weight %) | | | 1.5 ├────── | ──────┤ 2.5 | ∿ 3.0 ├────┤ |
| Stoppage of the plant | | | | ├┤ ├┤ | ├┤ |

## 2. Results of the Performance Tests

a. Results of Maximum Load Test: The results of the maximum load test was as follows, in which we obtained very good results surpassing the design value.

Flue gas conditions (at the inlet of the No.2 absorber):

Gas flow rate : 146,000 Nm$^3$/h
Gas temperature : 170°C
Sulfur in oil : 2.5 — 3.0 wt%

Operating conditions:

Mole ratio of alkali agents supplied to the absorber : $Ca^{2+}/Mg^{2+} = 3.5 - 4$
Flow rate of circulating absorbent liquor : 1,260 m$^3$/h
pH of absorbent liquor : 5.3
pH in the oxidizer (1st stage) : 3.5
pH in the oxidizer (2nd stage) : 2.5
Moisture of by-product gypsum : 9 wt%

Result of measurement of efficiency:

SOx concentration at the inlet of the absorber (dry) : 1,570 ppm
SOx concentration at the outlet of the absorber (dry) : 79 ppm
Desulfurization efficiency : 95.0%
Guarantee value:
    SOx concentration at the inlet : 1,412 ppm
    SOx concentration at the outlet : 100 ppm
    Desulfurization efficiency : 93%

Particulate concentration at the inlet of the absorber (dry) : 0.190 g/Nm$^3$
Particulate concentration after reheating (dry): : 0.051 g/Nm$^3$
Guarantee value:
    Particulate concentraion at the inlet : 0.2 g/Nm$^3$

Particulate concentration after re-heating : 0.1 g/Nm$^3$

We found no scaling in an inspection to the inside of absorber during a stoppage of the plant, and so we could confirm that the scaling trouble could be mitigated by the presence of $MgSO_4$.

b. Results of Several Tests:

Relation between pH of Absorbent Liquor and Desulfurization Efficiency:
Relation between pH of absorbent liquor and desulfurization efficiency is shown in Figure 4 with a parameter of liquid-to-gas ratio.
Above data are for a 75% of gas load factor, and the desulfurization efficiency can be expected to be higher in a 100% load, because the contact of gas and liquid is expected to be more efficient.

Relation between Liquid-to-Gas Ratio and Desulfurization Efficiency:
Relation between the liquid-to-gas ratio and the desulfurization efficiency, in the condition that pH of the absorbent liquor is 5.5 and the gas load factor is 100%, is shown in Figure 5.

It is recognized that a high efficiency of desulfurization can be obtained with a small value of liquid-to-gas ratio in the Magnesium-Gypsum Process, compared with a lime scrubbing process in which a liquid-to-gas ratio of 10 — 20ℓ/Nm$^3$ is necessary in general.

The velocity of the reaction of desulfurization depends largely on a solubility of absorbent agent, and the higher the solubility of $SO_3^{2-}$ in the absorbent liquor is, the higher absorption efficiency can be obtained.

Relation between the solubility of $SO_3^{2-}$ and the $MgSO_4$ concentration in the absorbent slurry is shown in Figure 6. In this process, the solubility of $SO_3^{2-}$ is high, because $MgSO_4$ is contained in the absorbent liquor at a concentration of 50 g/ℓ.

This is exactly the reason why there exists an apparent difference in desulfurization efficiency between Magnesium-Gypsum Process, which contains $MgSO_4$ in the absorbent, and lime scrubbing process which does not apply $MgSO_4$.

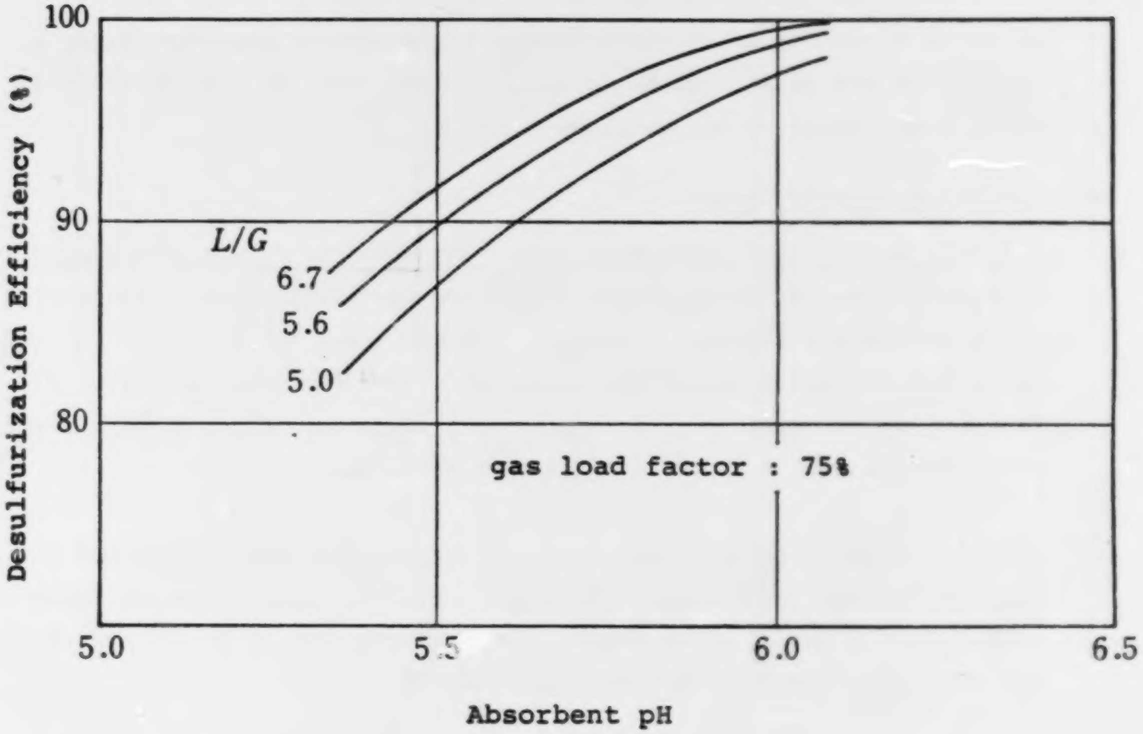


Figure 4. Relation between Desulfurization Efficiency and Absorbent pH

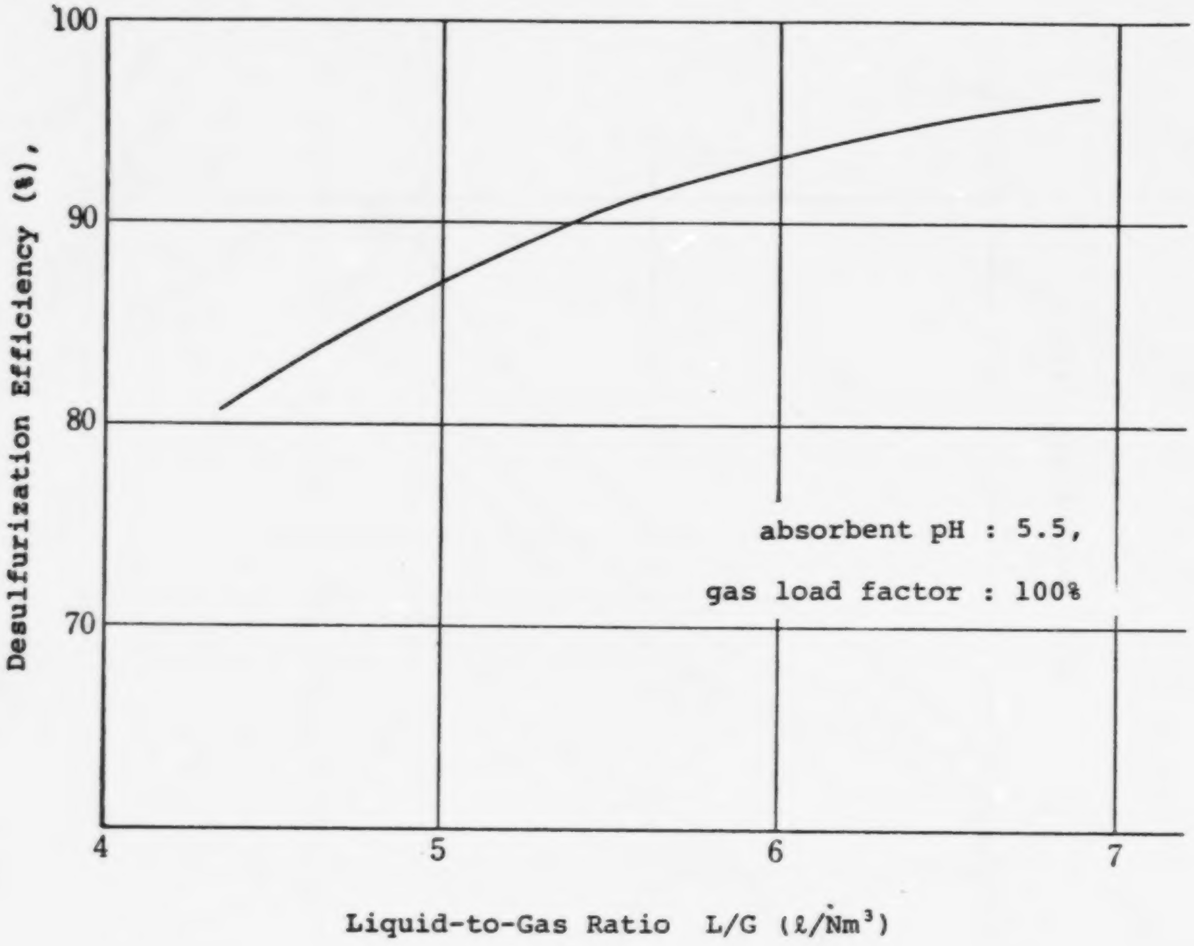


Figure 5. Relation between Desulfurization Efficiency and Liquid-to-Gas Ratio

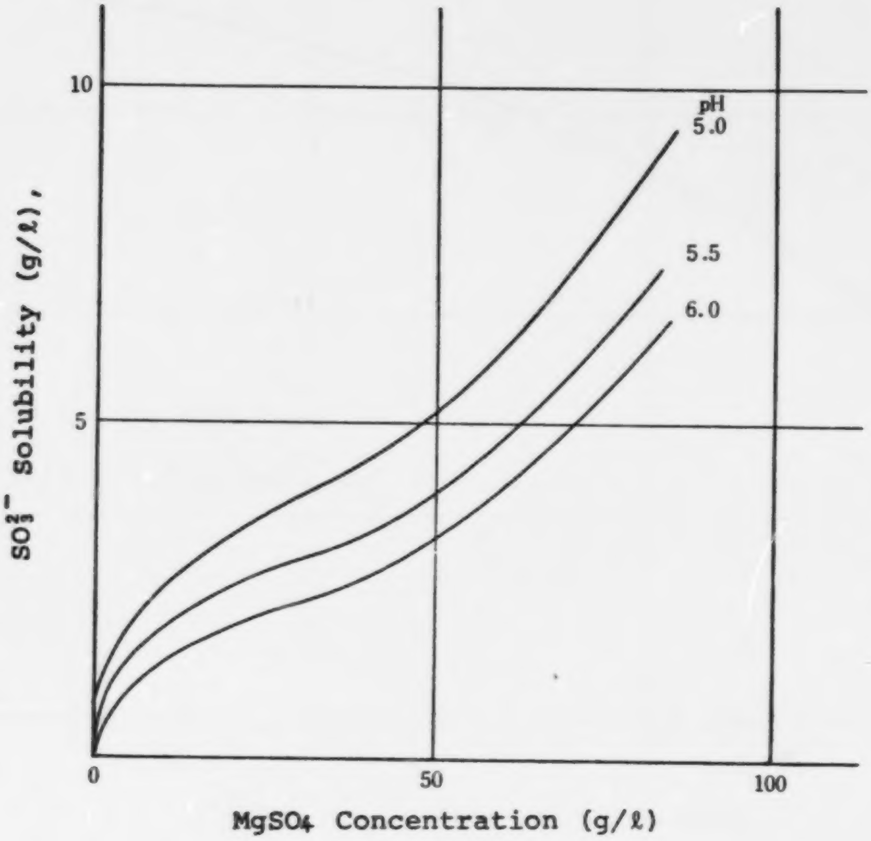


Figure 6. Relation between $MgSO_4$ Concentration and $SO_3^{2-}$ Solubility

## Relation between the Gas Load Factor and Desulfurization Efficiency:

Relation between the gas load factor and desulfurization efficiency with a parameter of liquid-to-gas ratio is shown in Figure 7, where pH of the absorbent liquor is 5.5.

Desulfurization efficiency tends downward as the gas load factor becomes lower if all other operating conditions are held constant.
However, in practice, the desulfurization efficiency becomes higher, since the flow rate of circulated absorbent liquor is kept constant irrespective of the gas load factor, resulting in the liquid-gas ratio becoming relatively larger as the gas load factor becomes smaller.

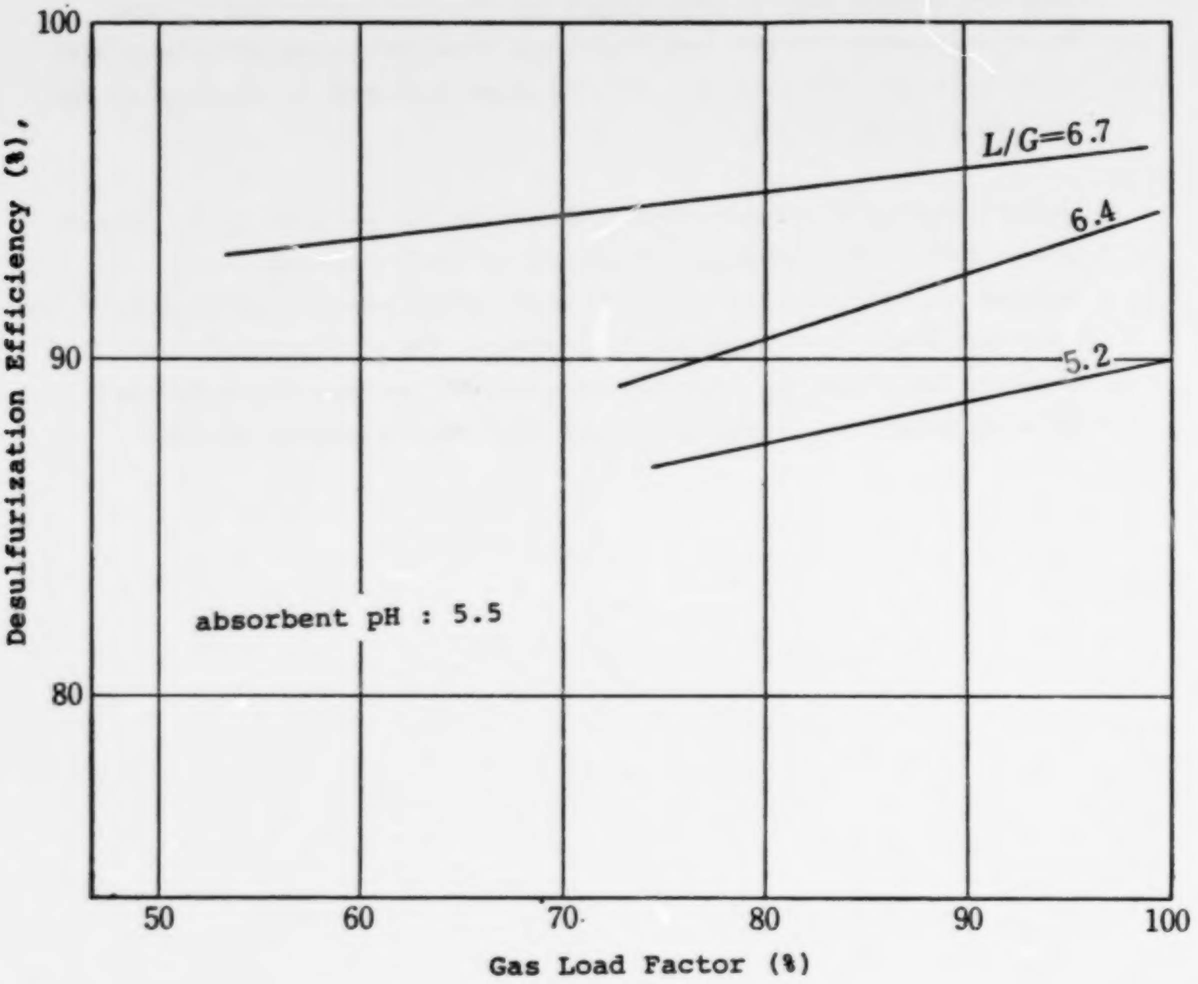


Figure 7. Relation between Desulfurization Efficiency and Gas Load Factor

## C. PROBLEMS AND SOLUTIONS IN THE TRIAL RUN

The trial run was successful and we had not so many major problems. Some problems we experienced in the trial run were as follows:

### 1. Scaling Trouble of the Mist Eliminator

When we inspected the inside of the equipment after 1,000 hours of operation, no scaling was found in the absorbers proper, in the piping around the absorber, in the raw material slurry section and in the mother liquor section, however, some scale mixed with carbon dust was found in the No.2 mist eliminator and in the No.2 drain tank including the attached piping.

We made an investigation of the factor of the scaling and the solution to avoid the scaling, which may disturb the continuous operation.
The mist eliminator was washed with mother liquor in order to prevent the adherence of mist.

According to our investigation, we found the factor of scaling as follows;

a. When the gypsum contained in a mother liquor as a saturated solution is mixed with the mist of absorbent liquor, solidification of gypsum occurs because a solubility of gypsum becomes lower.

b. The gypsum is generated by the following reaction between the sulfuric acid contained in mother liquor for washing and $CaSO_3$ contained in the mist of absorbent liquor.

$$CaSO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + SO_2$$

Considering the above phenomena, we tried to change a condition of operation, to make some modification of the equipment, etc., but we could not get a final solution.

We finally gave up the washing with mother liquor in the No.2 absorption section, and an intermittent washing method with industrial water was adopted.

Studying the optium quantity of washing water and the optimum interval of washing, we found it possible to wash the mist eliminator within the limits of the water balance of the process, which keeps no discharge of effluent liquor.

Good operation without any trouble of scaling has been maintained since then. On the other hand, in the No.1 absorption section, washing with mother liquor has been kept in operation without any trouble of scaling, because the composition of absorbent liquor in the No.1 absorption section is different from that of the No.2 absorption section due to a low gas load factor.

## 2. Clogging in a Chute of Pulverized Material Feeding Equipment

The chute provided between a screw conveyor and a bucket elevator and those provided between a bucket elevator and a service hopper were often clogged. However, the absorption section which is an essential part of the whole equipment, has never been stopped in operation, partly because the enough quantity of raw material slurry for several hours operation was stored in the alkali slurry tank.

It proved that the clogging was caused by inadequacy of the shape of the chute such as too large curvature, too small area of its cross section, etc.

Trouble of the clogging was solved by the following counter-plan.

a. Enlargement of the area of the cross section of the chute.

b. Decreasing the number and inclination of the curvatures.

c. Lining the chute with Teflon resin.

## 3. Clogging of a Filter-Cloth in a Centrifuge

Drop of the separation efficiency of centrifuges occured in two months from the beginning of the trial run. This process applies non effluent liquor system, therefore, the only way for the carbon dust to be taken out of the process is the mixing with the gypsum.

The drop of the separation efficiency of a centrifuges is caused by clogging of a filter-cloth with the carbon dusts.
In a normal operation, by-product gypsum has a liquid content of about 10% and can be handled easily, but the separation efficiency becomes lower gradually as the operation of the centrifuge repeats its batchwise operation, resulting in the increase of liquid content of the gypsum far over 10%.

In order to this problem, we tried to use several kinds of filter-cloths and compared their durability.

Fortunately we did find a filter-cloth which was superior in durability and could be re-used after a light cleaning, outside the centrifuge.

We solved the problem of clogging by using the new type of filter-cloth as mentioned above.

## D. RESULTS OF COMMERCIAL RUN

This plant has been maintained a commercial run in a good condition since March in 1976.
There were two times of stoppage for an annual inspection of the boilers, and the operability factor (hours the FGD plant was operated/boiler operating hours) of the FGD plant is 98 percent.

Other conditions of the operation are as follows:

| | |
|---|---|
| Gas load factor (average) | : No.1 20%<br>No.2 80% |
| SOx concentration, Absorber inlet | : 1,400 ppm (dry) |
| SOx concentration, Absorber outlet | : 100 ppm (dry) |
| pH-value of absorbent liquor | : 5 – 6 |
| The number of operators | : 1 person/1 shift<br>3 shifts a day |

This process is a closed cycle with no effluent liquor from the system. Only a leakage of sealing water from the stuffing box of the pumps or a drain water from the gas ducts are discharged outside without recovery, which are almost the same as fresh water in quality.

$Cl^-$ concentration in the system is about one thousand ppm.

By-product gypsum is used for cement additives.

As an electrostatic precipitator is not equipped in this plant, most of the carbon dusts contained in flue gas are mixed into the by-product gypsum. Therefore, there are some problems in the quality of gypsum when it is applied to the other uses such as wall board.

After long run, some worn areas have been observed in piping made of resin or in a control valve for slurry.

## E. ECONOMICS

The operating cost indicated in Table 3 is based on the tentative design of Magnesium-Gypsum Process for 500 MW coal fired power unit.
The capital investment is calculated on the basis of the domestic cost of Japan in 1976.

Basis:

Coal consumption, 1,372,000 tons/yr - 9,340 Btu/kwh.
Power unit on-stream time, 7,000 hr/yr.
Capital investment, $22,860,000 (without stack gas reheat).
Disposed gypsum in solid 160,000 tons/yr.
Cost of utility supplied from power plant is for the case of full load operation.

## Table 3 AVERAGE ANNUAL OPERATING COSTS FOR KAWASAKI MAGNESIUM GYPSUM PROCESS

(500 MW coal fired power unit, 2 % S in fuel)

| | Annual quantity | Unit cost, $ | Total annual cost, $ | Cost/ton of Coal consumption, $ | Cost/kwh mills |
|---|---|---|---|---|---|
| **DIRECT COSTS** (excluding cost for solid disposal) | | | | | |
| **Delivered raw material** | | | | | |
| **Lime** | 59,000 tons | 24.50/ton | 1,445,500 | 1.054 | 0.413 |
| **Magnesium hydroxide** | 990 tons | 120 /ton | 118,800 | 0.087 | 0.034 |
| **Conversion costs** | | | | | |
| **Operating labor and supervision** | 30,000 man-hr | 8.00/man-hr | 240,000 | 0.175 | 0.069 |
| **Utilities** | | | | | |
| **Process water** | 231 Mgal | 20 /Mgal$^b$ | 4,620 | 0.003 | 0.001 |
| **Electricity** | $72 \times 10^6$ kwh | 0.015/kwh$^b$ | 1,080,000 | 0.787 | 0.309 |
| **Maintenance** | | | | | |
| **Labor and material, 3 % of capital investment** | | | 685,800 | 0.500 | 0.196 |
| **Analyses** | | | 40,000 | 0.029 | 0.011 |
| **Subtotal conversion costs** | | | 2,050,420 | 1.494 | 0.586 |
| **Subtotal direct costs** | | | 3,614,720 | 2.635 | 1.033 |
| **INDIRECT COSTS** (excluding cost for solid disposal) | | | | | |
| **Average capital charges at 14.9 % of initial fixed investment** | | | 3,406,140 | 2.483 | 0.973 |
| **Overhead** | | | | | |
| **Plant, 17.5 % of conversion costs** | | | 358,824 | 0.262 | 0.103 |
| **Administrative, 11 % of operating labor** | | | 26,400 | 0.019 | 0.008 |
| **Subtotal indirect costs** | | | 3,791,364 | 2.764 | 1.084 |
| **Total annual operating costs, excluding costs for disposal of solids** | | | 7,406,084 | 5.399 | 2.117 |
| **Annual operating costs for off-site disposal of solids at $ 6/ton** | | | 960,000 | 0.700 | 0.274 |
| **Total annual operating costs, including cost for solid disposal** | | | 8,366,084 | 6.099 | 2.391 |

# II. INVESTIGATIONS RELATED TO DESULFURIZATION PROCESS

Since practical applications of desulfurization plants have been put into practice, many experiences of flue gas desulfurization processes have been obtained and the studies about the flue gas desulfurization process have been concentrated on some special problems.

Recently, the problems on the waste water and the quality of by-product gypsum have been regarded as more important problems than those on the desulfurization efficiency which was an important problem at first stage.

## A. TREATMENT OF THE EFFLUENT LIQUOR

### 1. Quantity of Effluent Liquor

It depends on a balance of water in the FGD process and an allowable level of concentration of the harmful impurities whether a discharge of effluent liquor from the sytem is necessary or not, and how much the quantity of effluent liquor is, if necessary.

The harmful impurities said above are classified into the following two kinds:

a. The harmful substances for the process, which may effect on a desulfurization efficiency, etc., when they reach a certain level of concentration... ..... $Cl^-$, $F^-$, $S_2O_6^{--}$, etc.

b. The harmful substances for the material, which may effect on a corrosion when they reach a certain level of concentration ......... $Cl^-$, $F^-$.

In general, it is seldom that the discharge of effluent liquor is necessary in order to maintain a balance of water in the system, except for the case when a pre-scrubber is completely separated from an absorber in the process.

It is possible to operate without discharging effluent liquor from a full load to a 1/3 load in the Magnesium-Gypsum Process, where a pre-scrubber is not provided at the upstream of an absorber.

Therefore, the factor to decide a quantity of effluent liquor is a level of concentration of the abovementioned harmful substances, especially that of $Cl^-$, which flows much into the system and is accumulated to a high concentration in the case of coal-fired power plant.

The effect of the accumulated $Cl^-$ is explained as follows:

## 2. Effect of $Cl^-$ on Desulfurization Efficiency

It is known that $Cl^-$ lowers the desulfurization efficiency in a lime scrubbing process.
We have made a basic experiment to confirm an effect of $Cl^-$ on the desulfurization efficiency in a magnesium scrubbing process compared with that in a lime scrubbing process.

The results are shown in Figure 8.
The conditions of the experiment were as follows:

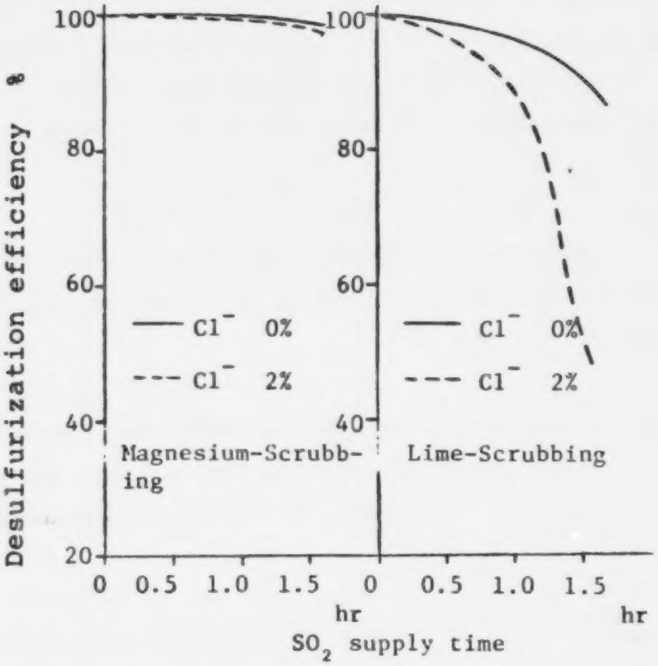
a. Method of test : Batch reaction

b. Supplied $SO_2$ gas : Concentration : 1,050 ppm
Flow rate : 4.5ℓ/min

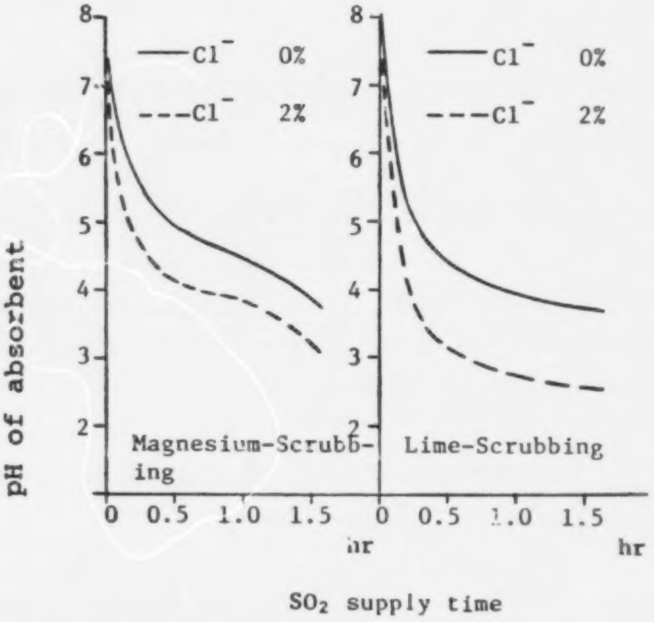
c. Initial quantity of the absorbent liquor before $SO_2$ gas is supplied : 330 g

d. Initial composition of the absorbent liquor

| | | Magnesium-Scrubbing | | Lime-Scrubbing | |
|---|---|---|---|---|---|
| $Cl^-$ | (wt.%) | 0 | 2 | 0 | 2 |
| $MgSO_3.6H_2O$ | (wt.%) | 0.8 | 0.8 | 0 | 0 |
| $MgSO_4.7H_2O$ | (wt.%) | 8.8 | 8.8 | 0 | 0 |
| $CaSO_4.2H_2O$ | (wt.%) | 10.9 | 10.9 | 10.9 | 10.9 |
| $CaSO_3.\frac{1}{2}H_2O$ | (wt.%) | 0 | 0 | 0.5 | 0.5 |



Relation between $SO_2$ supply time and desulfurization efficiency



Relation between $SO_2$ supply time and absorbent pH

Figure 8 Effect of $Cl^-$ on Desulfurization Efficiency

According to the results of the experiment, $SO_2$ absorption efficiency was conspicuously lowered by the effect of $Cl^-$ in the absorbent liquor of a lime scrubbing process. On the other hand, in the absorbent liquor of a magnesium scrubbing process, the absorption efficiency was hardly lowered in spite of the presence of $Cl^-$.

In addition, the fall of pH-value of the absorbent liquor owing to the presence of $Cl^-$ in a magnesium scrubbing process is much smaller than that in a lime scrubbing process.

The fall of absorption efficiency and pH-value of absorbent liquor by the effect of $Cl^-$ may be explained by the common ion effect, that is, $Cl^-$ surpresses the dissolution of $SO_3^{--}$, which carries out the absorption of $SO_2$.

The solubility of calcium compounds is very small and it is sensitive to an effect of $Cl^-$, so a small amount of $Cl^-$ has a remarkable effect on the desulfurization efficiency.

Meanwhile, the solubility of magnesium compoundsis very large (for example, the ratio of the solubility of $MgSO_3$ to that of $CaSO_3$ is over 100:1), so it is insensitive to a dissolution surpressing effect by $Cl^-$, and $Cl^-$ has not a practical effect on the desulfurization efficiency as is shown in the results of the experiment said above.

Therefore, in case that the flue gas from coal-firing which contains a lot of HCl is treated, it is necessary to install a pre-scrubber at the upstream of an absorber in order to absorb the HCl, or it is necessary to discharge a large amount of eff[illegible] liquor to prevent a rise of $Cl^-$ concentration in the absorbent liquor in a lime scrubbing process.

However, such countermeasures are not necessary in a magnesium scrubbing process, so it is more advantageous in this respect.

In addition, F has the same effect as $Cl^-$ on the desulfurization efficiency. However the effect of F is not so large as that of $Cl^-$, since the quantity of HF contained in a flue gas is not so much as that of HCl.

Concerning the effects of $Cl^-$ on materials, problems of pitting corrosion and stress corrosion cracking are important.

Recently, a new metallic material has been developed and put into practical use, which is suitably applicable to the handling of the liquid with high concentration of $Cl^-$ in a FGD plant.

On planning of some FGD plants for coal fired boiler, it is practically studied to keep $Cl^-$ concentration as high as 10,000 $\sim$ 20,000 ppm in the system in order to minimize the quantity of effluent liquor as far as possible.

As for the materials of the processing equipment and parts which require corrosive-proofing in such FGD plant, non-metallic materials such as resin, flake-glass lining, rubber lining, may be used for the parts contacting the liquor in the system, and special metallic materials may be used only for the parts where non-metallic materials are not applicable, such as a mechanical seal and shaft sleeve of pumps.

## 3. COD Value and $S_2O_6^{--}$ in Effluent Liquor

In relation to the harmful substance for the process, it is necessary to take account of the trace substances generated in the process itself besides those such as $Cl^-$ flowing into the FGD process from the outside of the system.

These trace substances may have a harmful effect on the process occasionally when they accumulate to some degree.

The following phenomena have become clear recently.

a. As an example of the substances generated in the process, $S_2O_6^{--}$ is generated in every FGD process: sodium-scrubbing process, magnesium-scrubbing process and calcium-scrubbing process.

b. $S_2O_6^{--}$ is generated in the case when $SO_3^{--}$ is oxidized by the air in the presence of $Fe^{+++}$.

c. The quantity of $S_2O_6^{--}$ to be generated depends both on the quantity of $SO_3^{--}$ oxidized and a concentration of $Fe^{+++}$.

$S_2O_6^{--}$ is inert for the reaction of desulfurization, and has seldom an effect on the process unless it is accumulated to a high concentration.

In case of discharging the effluent liquor, high COD value by $S_2O_6^{--}$ comes into question, because $S_2O_6^{--}$ is a substance which can not be oxidized easily by an ordinary method.

The folloiwng methods shown in Table 4 have been developed for the treatment of $S_2O_6^{--}$ to lower the COD value of effluent liquor.
Each method has some merits and demerits and can not be said to be completely satisfactory.

Meanwhile, we found that the quantity of $S_2O_6^{--}$ generated in the process decreases greatly when a reaction of oxidation of $SO_3^{--}$ takes place under such a high pH-value as 5.0 — 6.0, because the dissolved ferrous ion which plays a role of a catalyzer, is hardly present in the liquor under such a high pH-value.

Therefore, in the improved process of Magnesium-Gypsum process, which is explained later, the generation of $S_2O_6^{--}$ is surpressed by controlling pH-value to high degree. That is, most of $SO_3^{--}$ are oxidized in an absorber in which the pH-value is high, and the rest of $SO_3^{--}$ is oxidized by the air in an auxiliary oxidation tank in which the pH-value is kept 5 — 6.

Under the above condition, the quantity of $S_2O_6$ generated in the system can be controlled to a very small quantity, so it becomes possible to keep the COD value of effluent liquor lower than a specified regulation value in most case of discharging of the effluent liquor.

Table 4. METHODS OF TREATMENT OF THE SUBSTANCES HARD TO BE OXIDIZED

| No. | Classification | Contents | Problems and Characteristics |
|---|---|---|---|
| 1 | Decomposition by the sulfuric acid | Decomposition at, concentration of sulfuric acid;<br>$5 \sim 10\%$,<br>temperature; about 100°C | Suitable to a small capacity;<br>Equipment and operation are comparatively simple, but the consumption of sulfuric acid and caustic soda is large; |
| 2 | Thermal decomposition | Thermal decomposition at a temperature higher than 170°C | Strong corrosivity: Deposit of elemental S; Necessity of a pressurized vessel;<br>Large consumption of steam; |
| 3 | Electrolytic oxidation | Electrolytic oxidation with and electrodialysis membrane | Low current efficiency; Low electrolysis efficiency; Large dependence of current efficiency on the $Cl^-$ concentration; Necessity of pre-treatment; Suitable to the recovery in the system, but not suitable to the treatment of effluent stream; |
| 4 | Adsorption | Adsorption with an adsorbent agent such as resin, etc.<br>Used together with the methods 1,2,3,5 for a condensed liquor | Necessity of removal of Mg(Pre-treatment);<br>Suitable to an effluent stream of large quantity and low concentration; Complicated system |
| 5 | Drying-up | Drying-up by evaporation through a submerged combustion, spray combustion, etc. | Difficult handling and after-treatment of dried up Na-salt; High cost of the fuel when the waste heat is not available; |

## B. IMPROVEMENT OF THE QUALITY OF BY-PRODUCT GYPSUM

### 1. Use and Quality of Gypsum

As the flue gas desulfurization plant has made progress in its practical use, it has become a nation-wide problem to secure the use of the by-product gypsum from a desulfurization plant in Japan.

Main use of the gypsum by-produced from FGD plant are for cement additives and for the raw material of wall board at present, and a percentage of the latter is anticipated to increase in future.

In order to use the by-product gypsum from FGD plant as the raw material of wall board, the values which regulate the quality of gypsum for board, such as tensile strength at wet state, mixing water quantity, coagulation time, etc., are necessary to be within a certain range.
The main factors which have a remarkable effect on the values related to the quality are the size of crystal and the concentration of impurities.

In the Magnesium-Gypsum Process, $Mg(OH)_2$ is regenerated by the following reaction of regeneration, adding $Ca(OH)_2$ to the $MgSO_4$ generated in the system.

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow Mg(OH)_2 + CaSO_4.2H_2O$$

In the above reaction, only the gypsum like mud which consists of the crystal of very small size is generated in the case when a mole ratio of $MgSO_4/Ca(OH)_2$ is larger than 1.0, which is called "Perfect Regeneration".

In the standard Magnesium-Gypsum Process, the regeneration of $Mg(OH)_2$ under a condition where the mole ratio of $MgSO_4/Ca(OH)_2$ is smaller than 1.0, which is called "Partial Regeneration", is adopted in the basic design in order to prevent the generation of the gypsum with the small-sized crystal, which is troublesome to handle with and is inadequate to any use.

However, we have found a method to control the crystal size of gypsum generated in "Perfect Regeneration" process, where the mole ratio $MgSO_4/Ca(OH)_2$ is larger than 1.0, by an addition of some amount of the crystal of gypsum as a "seed crystal" to a regeneration tank and by regulation of a reaction temperature of regeneration.

An outline of our experiment on the above method is shown in the followings.

## 2. Experiment to Control the Size of Crystal of Gypsum

a. Condition and Results of the Experiment: Conditions of the experiment in a continuous reaction tank of small scale are shown in Table 5. Parameters regulated are as follows:

1) Feed rate of the "see crystal"
(weight of seed crystal/weight of gypsum to be regenerated) x 100(%)

2) Temperature of reaction (°C)

3) Mole ratio of $MgSO_4/Ca(OH)_2$ in regeneration reaction

The concentration of $MgSO_4$ in the mother liquor (the filtrate of separation of gypsum after the oxidation) supplied into the $Mg(OH)_2$ regeneration tank was regulated to be 5% for all the test run except for No.7, in which $MgSO_4$ concentration was regulated to be 10%.

The "seed crystal" was prepared for the test run by feeding into a mother liquor by a prescribed quantity.

$Ca(OH)_2$ to be supplied to $Mg(OH)_2$ regeneration tank was adjusted to be a slurry of 7% mixed with fresh water before the test.

An analysis of the particle size of "seed crystal" and the gypsum generated in each test run is shown in Table 6.

Table 5. CONDITION OF TEST RUN

| Test Run No. | Feed rate of the "seed crystal" | Temperature of reaction | Mole ratio of $MgSO_4/Ca(OH)_2$ |
|---|---|---|---|
| 1 | 87% | 58°C | 1.25 |
| 2 | 0 | 58 | 1.25 |
| 3 | 87 | 68 | 1.25 |
| 4 | 87 | 77 | 1.25 |
| 5 | 0 | 77 | 1.25 |
| 6 | 87 | 77 | 0.67 |
| 7 | 50 | 77 | 2.50 |

Table 6. ANALYSIS OF THE PARTICLE SIZE OF "SEED CRYSTAL" AND THE GYPSUM GENERATED

| Particle size (micron) | Test run No. | | | | | | | seed crystal |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| 0 ∿ 8 | 0.5 | 1.8 | 0.1 | 0.2 | 0.9 | 0.6 | 0.2 | 1.2 |
| 8 ∿ 16 | 8.5 | 10.6 | 3.5 | 2.4 | 9.6 | 7.9 | 4.3 | 14.4 |
| 16 ∿ 24 | 10.7 | 12.2 | 8.8 | 5.4 | 7.1 | 6.6 | 11.9 | 13.3 |
| 24 ∿ 32 | 14.2 | 5.4 | 4.5 | 8.4 | 4.5 | 6.7 | 9.4 | 11.1 |
| 32 ∿ 44 | 11.8 | 4.5 | 15.2 | 9.9 | 3.8 | 6.3 | 9.8 | 6.1 |
| 44 ∿ 53 | 17.5 | 13.8 | 17.2 | 19.5 | 11.2 | 14.6 | 16.5 | 24.8 |
| 53 ∿ 74 | 17.4 | 21.8 | 22.4 | 25.9 | 15.5 | 14.3 | 24.4 | 14.6 |
| 74 ∿ 105 | 12.5 | 14.0 | 13.9 | 17.4 | 18.6 | 8.0 | 15.2 | 7.7 |
| 105 ∿ 210 | 5.1 | 14.5 | 6.1 | 9.1 | 22.4 | 9.7 | 7.5 | 5.0 |
| 210 ∿ 297 | 1.4 | 0.9 | 0.9 | 1.3 | 5.8 | 4.3 | 0.5 | 0.9 |
| 297 ∿ 350 | 0.4 | 0.5 | 0.4 | 0.5 | 0.6 | 2.8 | 0.3 | 0.2 |
| over 350 | nil | nil | nil | nil | nil | 18.2 | nil | 0.7 |

b. Examination of the Results of Experiment:

Effect of Feed Rate of "Seed Crystal": The microscopic photographs of the crystal of gypsum generated in each test run are shown in Figures 9 — 13.

It is obvious that the crystal of gypsum supplied with "seed crystal" grows to a larger size than that without a supply of "seed crystal", making a comparison between the photographs for test run No.1 and No.2 or No.4 and No.5, which are the cases with and without a supply of "seed crystal" under the same condition of a mole-ratio and a reaction temperature.

In addition, the number of small particles of gypsum in the case with a supply of "seed crystal" proved much less than that in case without "seed crystal".

Effect of Reaction Temperature: An effect of a reaction temperature on the particle size of gypsum under a constant feed rate of "seed crystal" and a constant mole-ratio of the regeneration is shown in Table 7, where the particle size is found to become larger as a reaction temperature rises higher.

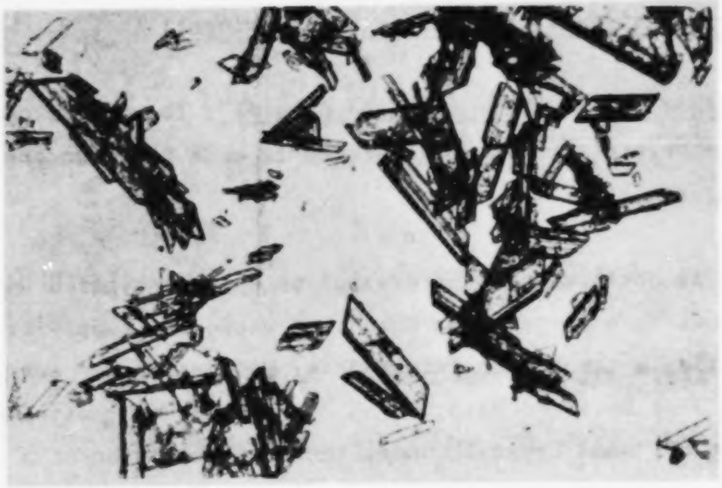


Figure 9 Crystal of Gypsum in Test Run No.1

Feed rate of the "seed crystal" : 87 %

Temperature of Reaction : 58°C

Mole ratio of $MgSO_4/Ca(OH)_2$ : 1.25

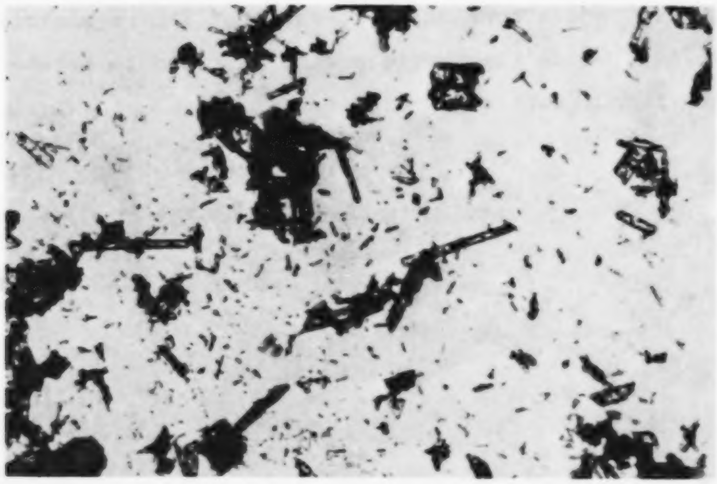


Figure 10 Crystal of Gypsum in Test Run No.2

Feed rate of the "seed crystal" : 0 %

Temperature of Reaction : 58°C

Mole ratio of $MgSO_4/Ca(OH)2$ : 1·25

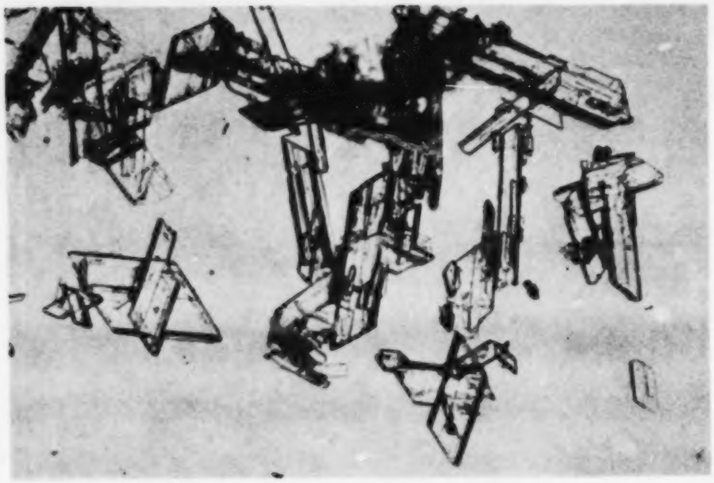


Figure 11 Crystal of Gypsum in Test Run No.4

Feed rate of the "seed crystal" : 87 %

Temperature of Reaction : 77°C

Mole ratio of $MgSO_4/Ca(OH)_2$ : 1.25

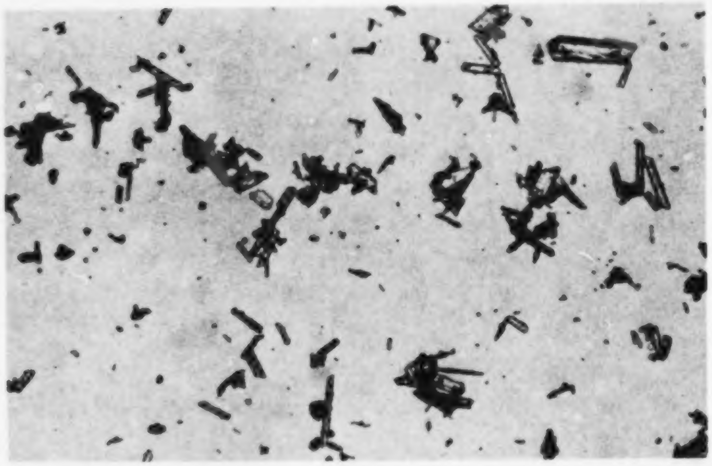


Figure 12 Crystal of Gypsum in Test Run No.5

Feed rate of the "seed crystal" : 0 %

Temperature of Reaction : 77°C

Mole ratio of $MgSO_4/Ca(OH)_2$ : 1.25

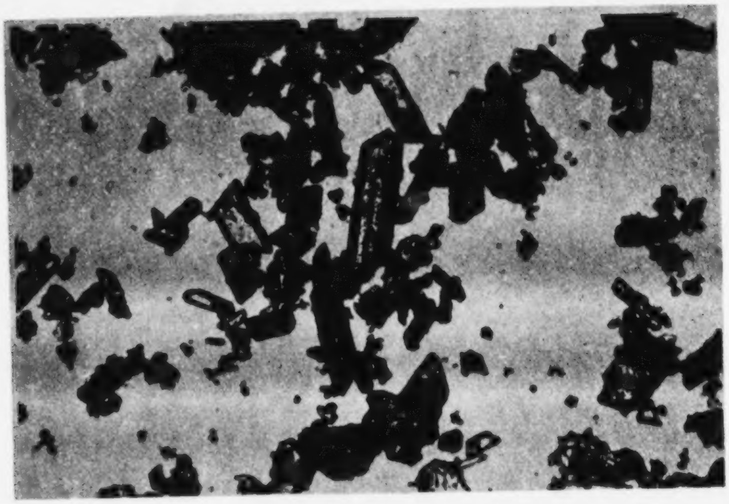


Figure 13 Crystal of Gypsum in Test Run No.6

Feed rate of the "seed crystal" : 87 %

Temperature of Reaction : 77°C

Mole ratio of $MgSO_4/Ca(OH)_2$ : 0.67

Table 7. RELATION BETWEEN THE REACTION TEMPERATURE AND THE PARTICLE SIZE OF GYPSUM

| Test run No. | Reaction Temperature | Weight ratio of particles less than 20 micron | Diameter of particle at weight ratio of 50% |
|---|---|---|---|
| "seed crystal" | | 24% | 41 micron |
| 1 | 58°C | 16% | 46 micron |
| 3 | 68°C | 8% | 50 micron |
| 4 | 77°C | 5% | 58 micron |

Effect of Mole-Ratio of Regeneration: It is found that the number of particles of small size in the case of a smaller mole-ratio of regeneration is more than that in the case of a larger mole-ratio, making a comparison between the photograph for test run No.4 and No.6, in which the mole-ratio is 1.25 and 0.67 under the same condition of a feed rate of "seed crystal" and a reaction temperature.

# III. NEW MAGNESIUM-BASE DOUBLE ALKALI PROCESS

## A. DESCRIPTION OF THE NEW PROCESS

We have recently established a new magnesium-base double alkali process, improving the standard Mg-Gypsum Process.
The new process is characterized by "Perfect Regeneration" in the process, that is, in the following reaction of regeneration in which $Mg(OH)_2$ is regenerated by addition of $Ca(OH)_2$ to $MgSO_4$ generated in the system,

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow Mg(OH)_2 + CaSO_4.2H_2O$$

a mole-ratio of the reactants supplied into a regeneration tank is regulated to be $MgSO_4/Ca(OH)_2 \geq 1.0$, therefore, all the $Ca(OH)_2$ supplied into a regeneration tank are changed into $Mg(OH)_2$ and $CaSO_4.2H_2O$, so, $Ca(OH)_2$ is not present in the liquor supplied to an absorber from the regeneration tank.

On the contrary, "Partial Regeneration" in which a mole-ratio of regeneration is regulated to be $MgSO_4/Ca(OH)_2 < 1.0$, and the liquor or alkali material supplied to an absorber from the regeneration tank contains $Ca(OH)_2$ as well as $Mg(OH)_2$, has been adopted in the standard Mg-Gypsum Process, and the mole-ratio of regeneration has been regulated to be $MgSO_4/Ca(OH)_2 = 1/3 \sim 1/4$ in order to obtain the by-product gypsum with a favorable size of particles.

A comparison between "Perfect Regeneration" and "Partial Regeneration" is shown in Table 8. According to the comparison, it is found that "Perfect Regeneration" is superior to "Partial Regeneration".

As shown above, "Perfect Regeneration" is a process in which the most of the advantages of a double alkali FGD process are fully made, and it can be applied in practice at once, if only its conventional disadvantage of generating the gypsum with a very small particle size is overcome.

Table 8. COMPARISON BETWEEN "PERFECT REGENERATION" AND "PARTIAL REGENERATION"

| | PERFECT REGENERATION | PARTIAL REGENERATION |
|---|---|---|
| Mole-ratio of regeneration | $MgSO_4/Ca(OH)_2 \geqq 1.0$ | $MgSO_4/Ca(OH)_2 < 1.0$ |
| Absorption efficiency | Absorption efficiency is better, as the absorbent agent is only the Mg-salt which has a high solubility and the pH-value of absorbent liquor is higher. | Absorption efficiency is a little lower, as the absorbent agent is a mixture of Mg-salt and Ca-salt which has a low solubility and the pH-value of absorbent liquor is lower. |
| Scaling | There is less fear of scaling, as all the Ca-compounds change into $CaSO_4.2H_2O$ before entering into an absorber, and the new generation of $CaSO_4$ $.2H_2O$ does not occur in the absorber.<br>So, an operation under a high pH-value in absorber is possible. | There is more fear of scaling, as some $Ca(OH)_2$ are supplied into an absorber and changed into $CaSO_4.2H_2O$ by oxidation.<br>So, an operation under a low pH-value in absorber is necessary to prevent the scaling. |

As has been previously mentioned, we have found a method to obtain the gypsum with a favorable size of particles even in "Perfect Regeneration" by addition of "seed crystal" and by control of the temperature in the regeneration.

So, it has become possible to establish a new magnesium-base double alkali process applied with "Perfect Regeneration".
A typical example of the new process is shown in the followings.

## B. DESIGN EXAMPLE OF THE NEW PROCESS

This example is for a flue gas desulfurization plant for a coal-fired boiler in a power station in Japan.
The "Perfect Regeneration" is applied in the Process.

### 1. Flow Diagram of the Process

The flow diagram of the process is shown in Figure 14.
All the $Ca(OH)_2$ change into $Mg(OH)_2$ in the regeneration tank "9" by a reaction with $MgSO_4$, so the contents of the alkali slurry tank "10" are $Mg(OH)_2$, $MgSO_4$ and $CaSO_4.2H_2O$.

The oxidation tank "11" is much smaller than an oxidizer in the standard Mg-Gypsum Process, because there is no $CaSO_3$ in the absorber "2", and it is not necessary to oxidize the calcium compounds.
Besides, most of $MgSO_3$ and $Mg(HSO_3)_2$ are oxidized in the absorber and the oxidizing load is expected to be much lighter.

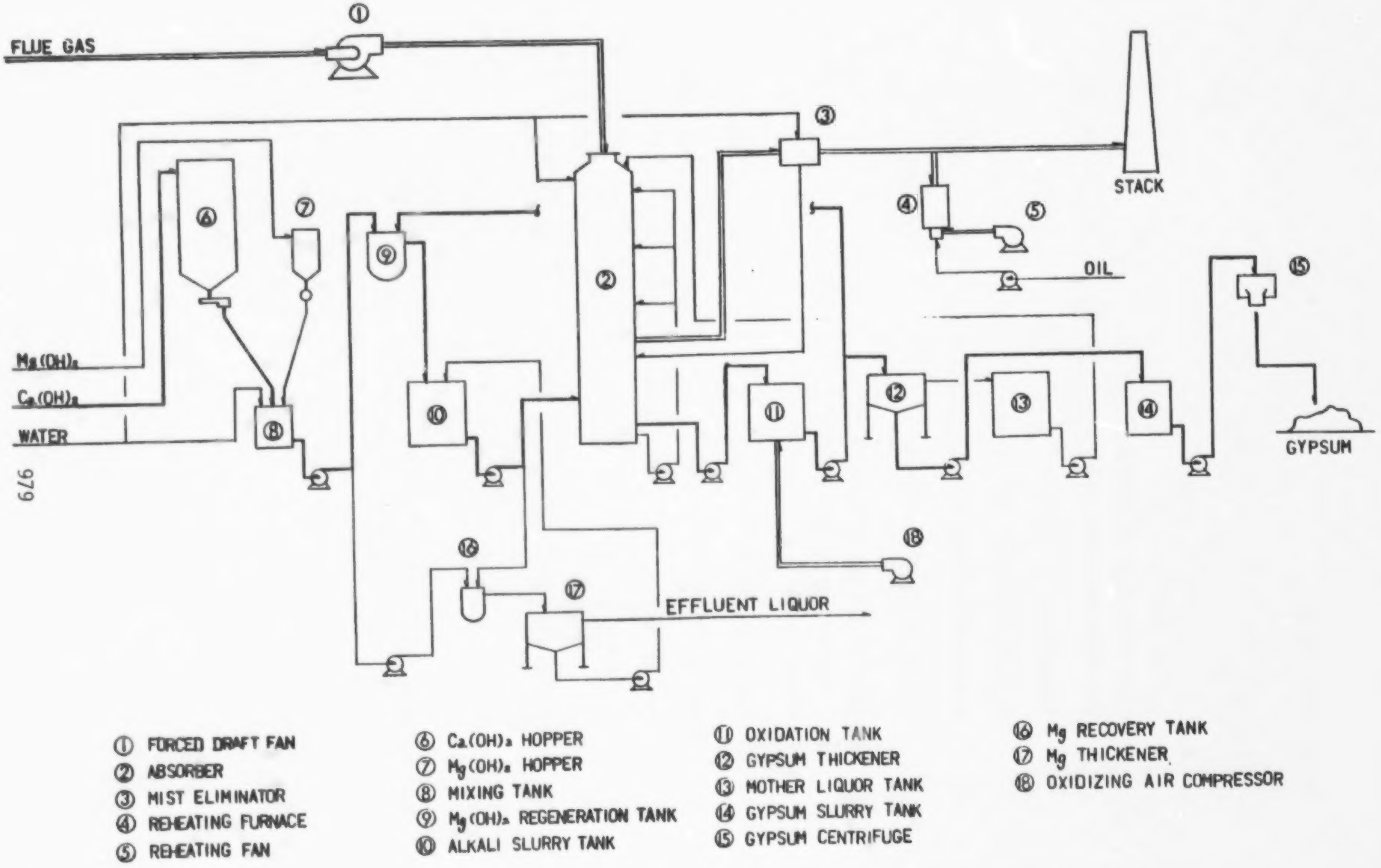


Figure 14 Flow Diagram of the New Magnesium-Base Double Alkali Process

## 2. Design Conditions

a. Out put : 175 MW

b. Fuel : Coal

c. Absorber inlet gas condition
   - Gas flow rate (wet base) : 610,000 $Nm^3/h$
   - Temperature : 137°C
   - $SO_2$ concentration (dry base) : 350 ppm
   - Particulate concentration (wet base) : 40 $mg/Nm^3$
   - Cl concentration in coal : 290 ppm

d. Absorber outlet gas condition
   - $SO_2$ concentration (dry base)
     - design value : 10 ppm
     - guarantee value : 20 ppm
   - Desulfurization efficiency
     - design value : 97%
     - guarantee value : 94%

e. Gas temperature after reheating : 137°C

f. Effluent liquor flow rate : 1,500 kg/h

g. Effluent liquor COD : 90 ppm

# TECHNICAL AND ECONOMIC FEASIBILITY OF SODIUM-BASED $SO_2$ SCRUBBING SYSTEMS

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## ABSTRACT

Sodium-based scrubbing utilizing commercial soda ash, trona ore, and process waste liquors containing soda ash has been demonstrated to be an effective means of sulfur dioxide removal. It is especially applicable to utility boiler applications in the Eastern states where stringent state regulations require low $SO_2$ and particulate emission levels. A soluble salt scrubbing system offers the advantages of very high removal efficiency combined with superior entrainment removal capabilities to minimize the contribution of entrainment to particulate emissions.

The Company's extensive experience with single and double-alkali sodium-based flue gas desulfurization (FGD) systems is reviewed. The operating advantages of these systems have resulted in demonstrably higher availabilities than exhibited by conventional lime/limestone systems. Comparative economics are presented and indicate that the sodium systems are competitive and can be less costly than the conventional systems for many cases. Costs per ton of coal for the various FGD alternatives indicate significant potential savings when compared to the use of low sulfur coal.

# TECHNICAL AND ECONOMIC FEASIBILITY OF SODIUM BASED SULFUR DIOXIDE SCRUBBING SYSTEMS

## Introduction

The passage of the Clean Air Act Amendments in 1971 and the increasingly high cost and questionable availability of oil have provided industry substantial motivation to develop technologies to deal with sulfur dioxide emissions. Of the many technologies developed, the most widely used systems utilize lime and limestone as chemical reagents. The many operating problems of these conventional lime/limestone systems are well publicized. These problems motivated FMC to explore the use of sodium chemicals for sulfur dioxide absorption. The technical and economic feasibility of these systems is the subject of this paper.

## Process Development

The original system was developed at FMC's plant in Modesto, California and uses a sodium solution to react with the $SO_2$ to produce sodium sulfite, bisulfite and sulfate for disposal. This "single-alkali" system is further described subsequently. The single-alkali system is particularly applicable to small installations, installations which have low concentrations of $SO_2$, or those plants which have caustic waste streams readily available. The initial work at Modesto formed the basis for the single-alkali sodium scrubbing system which has been installed at FMC's soda ash plant in Green River, Wyoming. At this plant there are waste streams available with sufficient sodium values to remove the desired $SO_2$ from the flue gas. The spent liquor is ponded with the rest of the plant blowdown. This type of installation is the simplest and least capital cost intensive of the FGD systems available.

The high cost of sodium chemicals at Modesto prompted FMC to investigate ways to transfer the absorbed sulfur dioxide from a sodium chemical to a less expensive carrier, calcium. Experimentation led to the development of a process in which lime is added to the spent liquor causing a reaction to occur which regenerates most of the sodium values for reuse. This patented "double-alkali" process decreases chemical costs significantly and minimizes potential disposal problems. The double-alkali process has been increasingly accepted as a technical and economically feasible solution to the sulfur dioxide emission problem.

## Process Description

### Single-Alkali

A schematic of the single-alkali process is presented in Figure I. Sulfur dioxide is absorbed in a solution containing sodium sulfite ($Na_2SO_3$), sodium bisulfite ($NaHSO_3$), and sodium sulfate ($Na_2SO_4$). As $SO_2$ is absorbed, the sodium sulfite is converted to sodium bisulfite and a very small percentage is oxidized to sodium sulfate. A bleed stream is taken from the recirculation system at the same rate that the $SO_2$ is being collected. The bleed stream can then be further processed through neutralization to eliminate the sodium bisulfite and aeration to convert the sodium sulfite to sodium sulfate if it's necessary to lower the chemical oxygen demand. Neutralization and aeration may be necessary to allow disposal into other wastewater treatment facilities or waste ponds.

### Double-Alkali

A process schematic of the double-alkali system is presented in Figure II. As can be seen by comparing Figure I and Figure II, the $SO_2$ absorption loops for single and double-alkali systems are virtually identical. In a double-alkali system, however, the bleed stream is further processed in the regeneration loop where the sodium bisulfite is reacted with slaked lime ($Ca(OH)_2$) in a low residence time agitated tank. The reaction of lime and sodium bisulfite regenerates sodium sulfite which is returned to the recirculation loop for reuse. Calcium sulfite ($CaSO_3$) which is precipitated is fed from the lime reactor to the thickener where the solids are concentrated. The slurry from the thickener is pumped to vacuum filters where filter cake of approximately 60% solids is formed and washed to minimize entrained sodium values. Sodium consumption is thus reduced to approximately 2% to 5% of the $SO_2$ collected for many applications.

The scrubbing solution in the $SO_2$ absorption loop is normally controlled at a pH of 6 to 7 with 6.5 as a design point. Above a pH of 7, carbon dioxide absorption becomes significant and can lead to formation of calcium carbonate scale. Below a pH of 6, the increase in $SO_2$ vapor pressure reduces the system's ability to absorb $SO_2$. FMC uses a setpoint of 6.5 where the sodium sulfite-sodium bisulfite solution is highly buffered and can readily adapt to rapid changes in $SO_2$ concentrations while maintaining constant collection efficiency.

The formation of sodium sulfate, which cannot be readily regenerated to recover sodium values, is inhibited through the use of a high ionic strength scrubbing solution that contains a

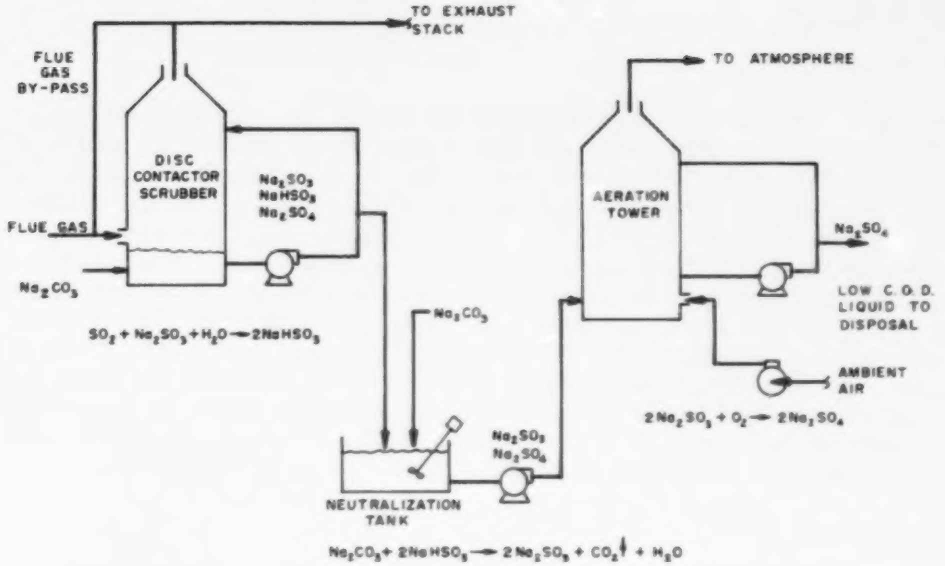

FIGURE I

SINGLE - ALKALI PROCESS SCHEMATIC

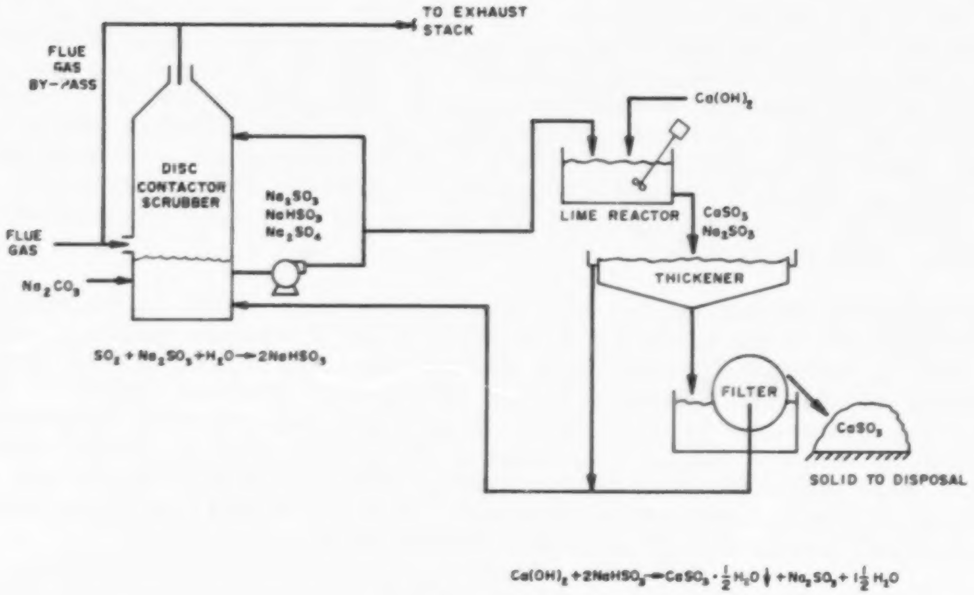

FIGURE II

CONCENTRATED DOUBLE - ALKALI PROCESS SCHEMATIC high sulfate concentration. This inhibits oxidation from sulfite to sulfate and minimizes the consumption of sodium chemicals. FMC's scrubber designs have also been optimized to provide for minimal oxidation.

The regeneration of sodium values takes place in the lime reactor where the reaction of sodium bisulfite with lime is controlled at a pH of 8.5. This is effectively the titrimetric endpoint for sodium bisulfite and operating at this pH insures excellent response of the control system. This greatly reduces the possibility of introducing excess lime. In addition to poor chemical utilization, excess lime would result in poor filter cake quality and substantially higher operating costs.

Maintaining high dissolved sulfite concentrations in the scrubbing liquid results in dissolved calcium concentration considerably below saturation levels, thereby eliminating the formation of calcium scale. Calcium scaling is the major contributor to the operating problems experienced by conventional lime/limestone systems.

## Technical Advantages

Sodium scrubbing systems have significant technical advantages which result in lower cost for many applications. These advantages are described below.

1. Reliability. A soluble scrubbing system is inherently more reliable than a calcium slurry system. FMC's experience to date clearly illustrates this fact. Reliabilities have in almost all cases exceeded the 90% requirement often specified. The prime reason for this is the elimination of the calcium scale which has caused the majority of the problems for conventional systems. To date no FMC system has been shut down due to calcium scaling.

2. Simultaneous $SO_2$ and particulate removal. Sodium scrubbing systems provide the flexibility to simultaneously control sulfur dioxide and particulate. Alternatively, particulate control systems can be provided which can be subsequently adapted for $SO_2$ control.

3. Lower maintenance. The use of a buffered solution rather than a slurry for scrubbing greatly reduces corrosion and erosion in the scrubber and associated equipment and piping. This combined with the no-scaling characteristics previously discussed leads to considerably reduced maintenance costs.

4. Manageable waste. The filter cake produced by the double-alkali system differs significantly from that produced by lime or limestone processes. As can be seen in the illustrations (Figures III to VI) the double-alkali precipitate is a granular material, rather than a sludge. It is moved by conveyor belts from the vacuum filters to transfer points. It can be conveyed directly to a disposal container or allowed to fall on the ground for future removal by front-end loader and truck. The material does not go into a slurry form upon mechanical agitation. The mechanical stability allows the precipitate to be moved and landfilled using conventional wide-track equipment. Successful landfill operations are presently being conducted in two states.

   Local regulations for landfilling the filter cake may or may not require the area to be lined. Linings may be required in locations where the soil is porous or the ground water level high. Fixation is not required to provide mechanical stability.

5. Low power requirements. Sodium systems provide the opportunity to operate at comparable pressure drops and at significantly lower liquid-to-gas ratios than those utilized in conventional lime/limestone systems. Total power consumption can be as low as 40% of other systems.

6. High $SO_2$ collection efficiencies. $SO_2$ collection efficiencies of up to 99% have been demonstrated. High collection efficiencies often permit partial bypass of the flue gas for reheat.

7. Ease of operation. A highly satisfactory control system package has been developed and demonstrated. The design of this package is predicated on the system being operated by "typical" boiler room operators and not engineers.

## Operating Experience

Figure VII summarizes major installations by FMC. Installations thus far range up to 265 Mw equivalent. FMC's experience in sulfur dioxide control began with the completion of the original installation at FMC's Modesto chemical plant. The installation of this system was dictated by adverse ambient conditions existing in the area. The unit is a 30 Mw equivalent system which has been in operation since late 1971. While not completely representative of the design FMC would utilize today, the system has demonstrated an extremely high degree of reliability in an application which experiences significant fluctuations in $SO_2$ conditions. Since December of 1971, this system has been available in excess of 95% of the time. FMC's largest non-utility

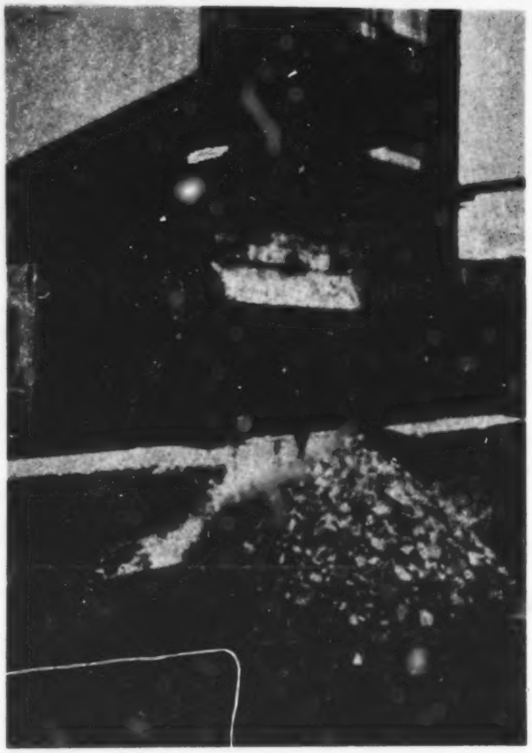

FIGURE III

Conveyor discharge into disposal container at Firestone Demonstration Plant.

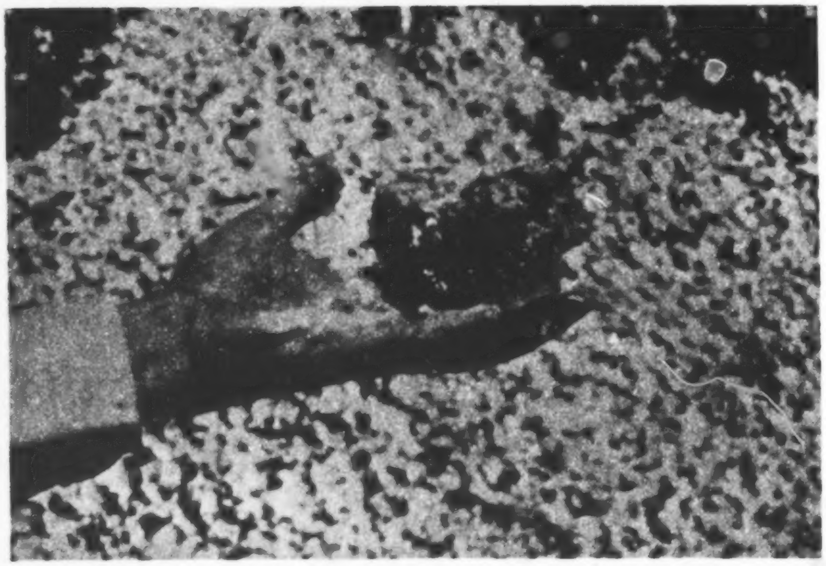

FIGURE IV

Sample of filter cake at Firestone landfill.

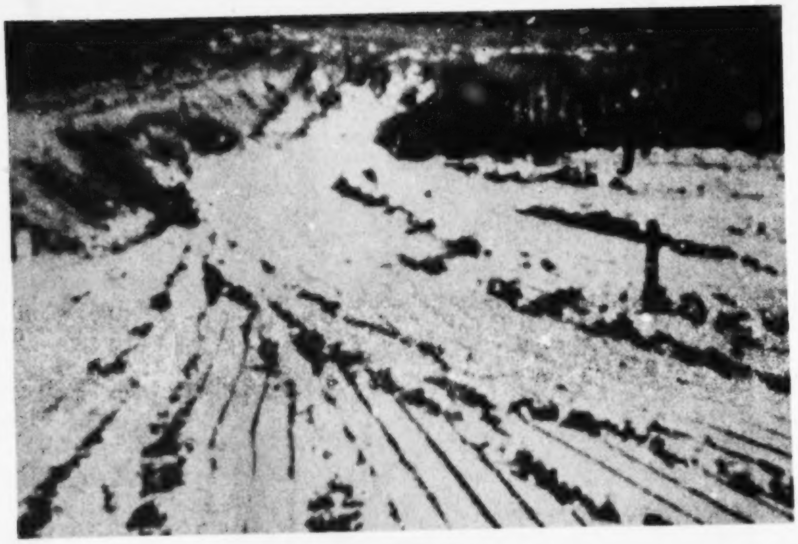

FIGURE V

Landfill area at Firestone (note dozer tracks in right foreground).

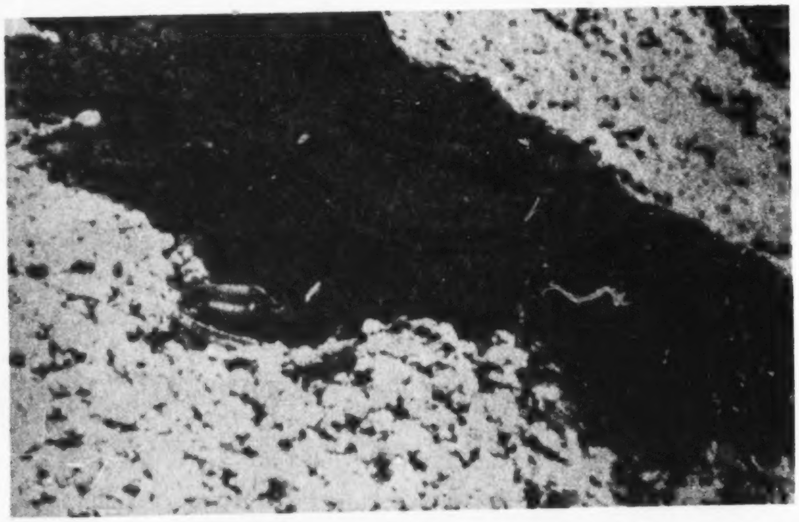

FIGURE VI

Climbing a recently dumped three-foot deep pile of waste material demonstrates physical stability.

**FIGURE VII.** Major Installations

| Installation | Type | Capacity Saturated cfm-Mw Equivalent lbs/hr Steam | Start-up | Performance |
|---|---|---|---|---|
| FMC Industrial Chemical Div.<br>Modesto, CA | $SO_2$ and Kiln Dust | 30,000 cfm - 30 Mw | 12/71 | 99% $SO_2$ Removal<br>95%+ Availability |
| Canton Textile<br>Canton, GA | $SO_2$ and Flyash | 30,000 cfm - 10 Mw | 6/74 | 70% $SO_2$ Removal<br>90%+ Availability |
| Firestone Tire & Rubber<br>Pottstown, PA | $SO_2$ and Flyash | 10,000 cfm - 3 Mw | 1/75 | 90% $SO_2$ Removal<br>94% Availability |
| Caterpillar Tractor<br>Mossville, IL | $SO_2$ and Flyash<br>3.2%S Coal | 240,000 cfm - 55 Mw<br>460,000 lbs/hr | 10/75 | 90% $SO_2$ Removal |
| E. Peoria, IL | $SO_2$ and Flyash<br>3.2%S Coal | 320,000 cfm - 100 Mw<br>870,000 lbs/hr | 10/77 | 90% $SO_2$ Removal |
| Mapleton, IL | $SO_2$ and Flyash<br>3.2%S Coal | 640,000 cfm - 200 Mw<br>1,800,000 lbs/hr | 11/77 | 90% $SO_2$ Removal |
| FMC Industrial Chemical Div.<br>Green River, WY | $SO_2$ Control<br>Up to 1.3%S Coal | 660,000 cfm - 150 Mw<br>1,300,000 lbs/hr | 6/76 | 90% $SO_2$ Removal |
| Southern Indiana Gas and<br>Electric Company<br>Evansville, IN | $SO_2$ Control<br>Up to 4.5%S Coal | 840,000 cfm - 265 Mw<br>1,850,000 lbs/hr | 1/79 | 85% $SO_2$ Removal |

double-alkali installations to date are for the Caterpillar Tractor Co. The initial unit is located in Mossville, Illinois, and has been in operation since October, 1975. A smaller installation has been operating at Firestone Tire & Rubber Company's Pottstown, Pennsylvania plant since January, 1975. Both of the above installations have demonstrated the disposability of the filter cake generated by the double-alkali process.

In spring of 1976, FMC started up its largest single-alkali scrubbing system thus far. It consists of two 330,000 acfm disc contactor scrubbers (Figure VIII) on the new pulverized coal-fired boilers installed at FMC's soda ash plant in Green River, Wyoming. The boilers are two 650,000 lbs/hr units followed by high efficiency electrostatic precipitators. The scrubbers are designed to remove in excess of 90% of the sulfur dioxide at a low pressure drop. These scrubbers are representative of those which are being used by FMC in utility applications.

In late 1976, FMC was awarded its first contract for a utility double-alkali flue gas desulfurization system. This system will be installed at Southern Indiana Gas and Electric Company's A. B. Brown Unit No. 1 Station. The award of this contract was significant in that it was based on the lowest evaluated cost as compared to conventional lime and limestone systems.

One of the key detriments to the further commercialization of sodium based systems, especially double-alkali systems, is the mistaken contention that the higher chemical cost of thesw systems will make them noncompetitive when compared to lime/limestone systems. FMC believes that for many applications the economics of sodium based systems are competitive when all aspects of costs are considered. A complete cost evaluation must include factors such as maintenance, chemical storage and handling cost, operability, system availability, and disposal cost. In the following section, the costs of sodium based systems as compared to limestone systems are presented. These costs are also related to coal costs since a majority of utility and non-utility applications consider low sulfur coal as an alternative to flue gas desulfurization systems.

## Economic Comparisons

Annualized costs of single-alkali, double-alkali, and limestone scrubbing systems for a 500 Mw utility power station are presented and compared with the higher cost of low sulfur coal. Assumptions made in these calculations include:

Load Factor: 65%

HHV Coal: 12,000 Btu/lb
1.18 MM TPY coal fired

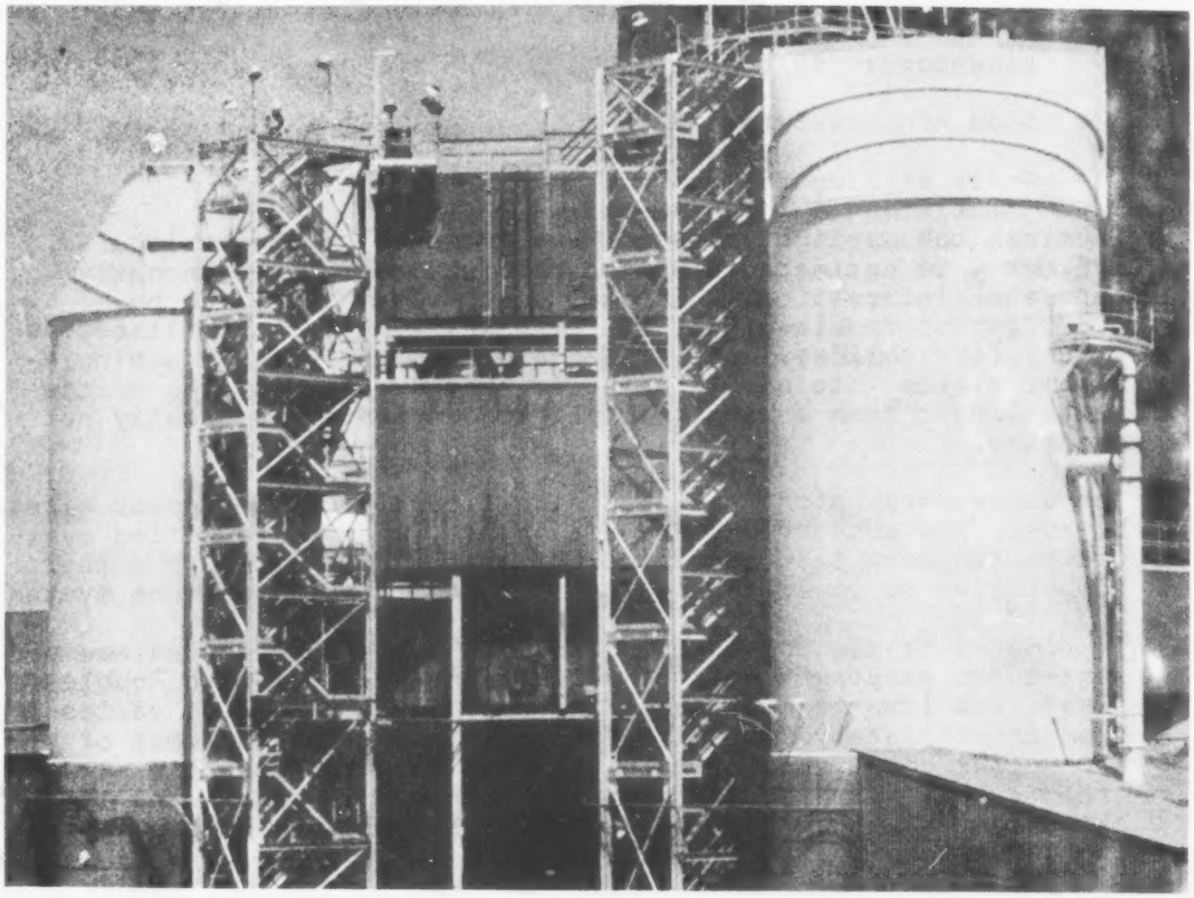

FIGURE VIII

Two 330,000 acfm Disc Contactor Scrubbers controlling $SO_2$ emissions from two 650,000 lbs/hr pulverized coal boilers.

Outlet $SO_2$ Concentration Required: 1.2 lbs/MM Btu

Capital Charge: 15%

Lime: $40/ton

Limestone: $5/ton

Soda Ash: $85/ton

Power at 2 cents/Kwh

Chemical consumption and power requirements of the various systems were estimated based on published data or internally generated information. Disposal costs were assumed to be $2.50/ton of double-alkali filter cake, $3.00/ton for limestone sludge (40% solids), and $4.75/ton of $SO_2$ removed for a single-alkali system. It should be noted that direct disposal of the bleed liquor from a single-alkali sodium system is usually not feasible.

The above assumptions can vary significantly for different sites; however, the assumptions are reasonable, and the resulting evaluation suggests that double-alkali system costs will be either competitive or lower than those of conventional limestone systems.

In Figures IX-XI, the cost for the FGD systems evaluated are presented for varying levels of sulfur content. For both double-alkali and limestone systems, the cost per ton of coal varies from approximately $4/ton to $9/ton. Given that the cost of low sulfur compliance coal in the East is often more than $10/ton greater than for high sulfur coal, both double-alkali and limestone systems often provide economic alternatives to the importing of western coal or foreign oil.

## FIGURE IX

### CAPITAL COST PER KW ($'S)

| Coal Sulfur Content | 2% | 3% | 4% | 5% |
|---|---|---|---|---|
| Double-Alkali | $32.50 | $35.00 | $37.50 | $40.00 |
| Non-regenerated Sodium | $21.00 | $22.50 | $24.00 | $25.50 |
| Limestone | $45.00 | $50.00 | $55.00 | $60.00 |

## FIGURE X

## ANNUALIZED COST FOR FLUE GAS DESULFURIZATION

| | Single-Alkali | Double-Alkali | Limestone |
|---|---|---|---|
| 2% Sulfur Coal | | | |
| Capital Cost | 10,500,000 | 16,250,000 | 22,500,000 |
| Reagent Cost | 4,203,000 | 1,263,000 | 297,400 |
| Capital Charge (15%) | 1,575,000 | 2,437,500 | 3,375,000 |
| Power Cost | 484,000 | 569,500 | 1,139,000 |
| Maintenance | 105,000 | 325,000 | 1,125,000 |
| Labor | 300,000 | 300,000 | 700,000 |
| Disposal | 143,000 | 261,000 | 590,000 |
| Total | 7,760,000 | 5,156,000 | 7,226,000 |
| 3% Sulfur Coal | | | |
| Capital Cost | 11,250,000 | 17,500,000 | 25,000,000 |
| Reagent Cost | 7,480,000 | 2,248,000 | 529,000 |
| Capital Charge | 1,688,000 | 2,625,000 | 3,750,000 |
| Power Cost | 484,000 | 569,000 | 1,140,000 |
| Maintenance | 112,500 | 350,000 | 1,250,000 |
| Labor | 300,000 | 300,000 | 700,000 |
| Disposal | 255,000 | 464,000 | 1,050,000 |
| Total | 10,320,000 | 6,556,000 | 8,419,000 |
| 4% Sulfur Coal | | | |
| Capital Cost | 12,000,000 | 18,750,000 | 27,500,000 |
| Reagent Cost | 10,759,000 | 3,236,000 | 758,000 |
| Capital Charge | 1,800,000 | 2,813,000 | 4,125,000 |
| Power Cost | 484,000 | 569,000 | 1,139,000 |
| Maintenance | 120,000 | 375,000 | 1,375,000 |
| Labor | 300,000 | 300,000 | 700,000 |
| Disposal | 376,000 | 668,000 | 1,512,000 |
| Total | 13,830,000 | 7,960,000 | 9,610,000 |
| 5% Sulfur Coal | | | |
| Capital Cost | 12,750,000 | 20,000,000 | 30,000,000 |
| Reagent Cost | 14,121,000 | 4,240,000 | 1,000,000 |
| Capital Charge | 1,912,000 | 3,000,000 | 4,500,000 |
| Power Cost | 484,000 | 569,000 | 1,140,000 |
| Maintenance | 127,000 | 400,000 | 1,500,000 |
| Labor | 300,000 | 300,000 | 700,000 |
| Disposal | 481,000 | 876,000 | 1,982,000 |
| Total | 17,430,000 | 9,390,000 | 10,820,000 |

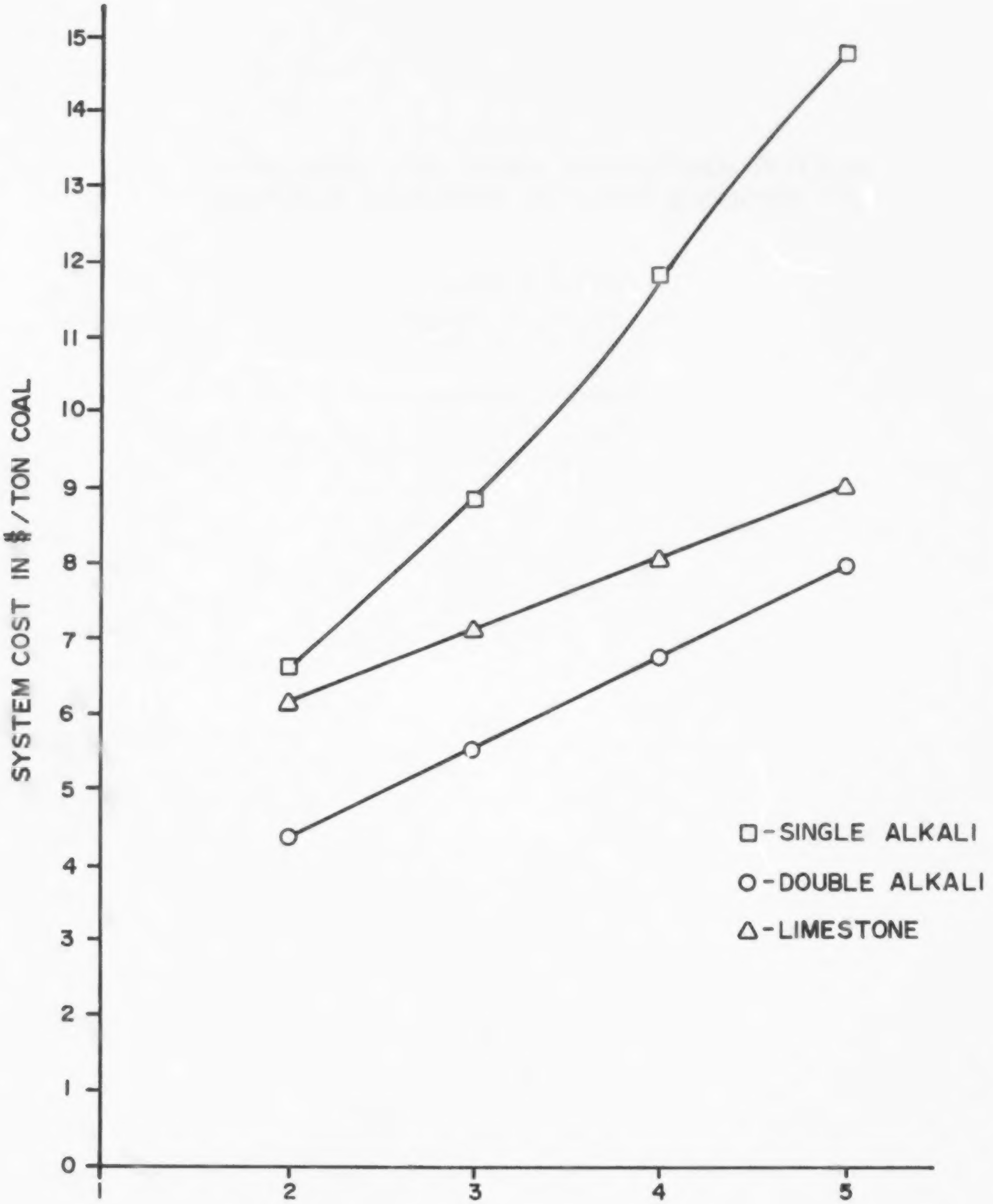

FIGURE XI:

COST OF FLUE GAS DESULFURIZATION
PER TON OF COAL CONSUMED

# SULFUR RECOVERED FROM $SO_2$ EMISSIONS AT NIPSCO'S DEAN H. MITCHELL STATION

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Allied Chemical Corporation
Morristown, New Jersey

**Roberto I. Pedroso**

Davy Powergas Incorporated
Lakeland, Florida

# SULFUR RECOVERED FROM $SO_2$ EMISSIONS AT NIPSCO'S DEAN H. MITCHELL STATION

HOWARD A. BOYER, ALLIED CHEMICAL CORPORATION
MORRISTOWN, NEW JERSEY
ROBERTO I. PEDROSO, DAVY POWERGAS INCORPORATED
LAKELAND, FLORIDA

## SUMMARY

Performance tests were completed and FGD operations are being continued by Allied Chemical Corporation for Northern Indiana Public Service Co. (NIPSCO) on a regenerable FGD facility for Unit No. 11, a 115 MW boiler burning 3% sulfur coal at NIPSCO's Dean H. Mitchell Station in Gary, Indiana. This fully integrated demonstration facility successfully removes 90% of the $SO_2$ from the entire flue gas output of Unit No. 11 and converts the recovered $SO_2$ to elemental sulfur at rates over 20 tons per day. The FGD system uses the Wellman-Lord $SO_2$ Recovery Process of Davy Powergas Inc. (DPG) and $SO_2$ Reduction to Sulfur Process of Allied Chemical.

Jointly funded by the U.S. Environmental Protection Agency (EPA) and NIPSCO, this fully integrated demonstration facility represents the first application of DPG's Wellman-Lord process in coal fired electric utility service and the first combination of the Wellman-Lord/Allied Chemical systems in flue gas desulfurization. It is also the first time that an experienced chemical firm has been engaged by an electric utility to manage its entire emission control facility and market the recovered products.

Performance tests were successfully completed on September 14, 1977, following a virtually uninterrupted period of operation which included 12 days at a flue gas volume equivalent to 92 MW and 84 hours at an equivalent of 110 MW. During this period, 91% of the $SO_2$ in the flue gas was removed while burning coal averaging 2.9% sulfur. About 204 long tons of elemental sulfur were recovered during this period.

Results were better than the performance criteria established for the acceptance test period. These criteria included:

1. Minimum 90% $SO_2$ removal.
2. Particulate emission not to exceed the Federal New Source Performance Standard (NSPS) for fossil fuel fired steam generators.
3. Daily average soda ash feed to make up for sulfite oxidation not to exceed 6.6 STPD.
4. Aggregate cost of steam, electricity, and natural gas at predetermined unit costs not to exceed $56 per hour.
5. Minimum 99.5% sulfur purity suitable for conversion to quality sulfuric acid by standard production practice.

Operation of the facility will continue through a demonstration year during which operating reliability will be tested over a wide range of conditions. As of September 19, 1977, 608 long tons of high purity sulfur have been recovered and sold to a nearby Allied Chemical plant where it is being consumed in the manufacture of sulfuric acid. Since the beginning of the performance tests, the reliability of the $SO_2$ emission control system has been very high, greater than 99%.

Performance at NIPSCO, to date and throughout the demonstration period, should firmly establish the commercial availability of a reliable and efficient regenerable FGD system in the U.S. There is growing evidence that electric utilities have a viable FGD option with conversion of stack gas $SO_2$ into a useful product. The concentrated $SO_2$ recovered by the Wellman-Lord process may be converted to either sulfur or sulfuric acid - avoiding the burdens and uncertainties of long-term sludge disposal.

## BACKGROUND

### Introduction

At the inception of this project, the Wellman-Lord $SO_2$ recovery process of Davy Powergas had demonstrated remarkable $SO_2$ removal efficiency and operating reliability on large oil-fired boilers in Japan. Allied Chemical had successfully recovered high quality elemental sulfur from $SO_2$ emitted by a Canadian metallurgical operation on a scale equivalent to a 2000 MW station burning 3% sulfur coal.

The 115 MW FGD facility now in operation at NIPSCO's Dean H. Mitchell Station was conceived by NIPSCO and EPA as an opportunity to significantly advance the state-of-the-art of regenerable FGD by combining two commercially proven processes to recover useful products from the emissions of a coal-fired boiler.

Under the basic project terms, EPA and NIPSCO jointly funded the installation while NIPSCO assumed all costs of operation. Davy Powergas undertook engineering, procurement, construction and performance testing of the complete system under contract to NIPSCO. Allied Chemical provided Davy Powergas with the process design for the conversion of $SO_2$ to elemental sulfur, as well as start-up services for the entire system.

In addition, NIPSCO engaged Allied to operate and maintain the facility and to market the chemical products during the demonstration period and on a continuing basis thereafter.

Construction was completed in the summer of 1976 and the first flue gas was accepted into the absorber on July 19, 1976. Following shakedown of the component parts in the FGD system, the FGD facility was idled for five months while repairs were made to NIPSCO's No. 11 boiler.

Start-up resumed on May 27, 1977, and performance test were successfully concluded on September 14, 1977, over the prescribed 12-day and 3-1/2 day test periods at 92 MW equivalent and 110 MW equivalent flue gas rates of 320,000 ACFM and 390,000 ACFM respectively.

## Project Structure

At an early date, NIPSCO the EPA recognized the need to assemble the specialized resources necessary to assure success of a chemical processing installation. An optimum combination of skills and resources were brought together in contractual arrangements between:

1. NIPSCO and DPG;
2. DPG and Allied Chemical;
3. Allied Chemical and NIPSCO.

## Operating Organizt on

With decades of sulfur pollution control services experience to client companies in the petroleum, detergent and other industries, Allied's participation as system manager at NIPSCO was a logical extension of its commitment to the recovery of useful sulfur products from potentially polluting wastes.

At the Mitchell Station, highly qualified professionals were selected from within Allied's organization for permanent assignment to all the supervisory functions in the facility. Operations and mechanics were recruited by Allied and trained at the site.

Allied's responsibilities include the full range of technical, maintenance, tests and inspection and process control functions (Exhibit 1) required for successful operation of the facility on a continuing basis.

Additional professionals were assigned to the project during the training period and throughout start-up to insure addquate round-the-clock supervision of initial operations through performance testing. The Allied permanent staff and start-up group supplemented by a Davy Powergas start-up team is illustrated in Exhibit 2.

During the demonstration year, which began September 16, 1977, technical specialists will assist the permanent Allied staff to optimize operations and make adjustments and modifications to assure efficient performance under changing load, fuel and other conditions. The permanent on-site organization is shown in Exhibit 3. It should be noted that the management and supervisory staff are sufficient to support a 500 MW FGD facility. Some additional maintenance men would be required.

## Product Marketing

Sale and distribution of useful products, whether sulfur or sulfuric acid, can be assured as an integral part of Allied Chemical's FGD system management commitment.

At NIPSCO, over 20 tons per day of sulfur are produced. It is shipped from the site as a liquid. The sulfur produced (608 long tons as of September 19, 1977) provides a fraction of the sulfur requirements of a nearby Allied Chemical plant where it is consumed in the manufacture of sulfuric acid. Likewise, the sodium purge salt, recovered from the Wellman-Lord system as dry granular product, will be channeled into such markets as the pulp and paper industry.

# PROCESS DESCRIPTION

## Wellman-Lord $SO_2$ Recovery

At NIPSCO, the Wellman-Lord process is composed of three major operating sections - $SO_2$ absorption, purge treatment and $SO_2$ regeneration.

In the $SO_2$ absorption section, residual fly ash in the flue gas is removed by water scrubbing. $SO_2$ is then removed by scrubbing with a solution of sodium sulfite. The chemicals contained in this solution remain completely dissolved throughout the absorber. Flue gas scrubbing with a clear solution, free from suspended solids, plugging and scaling, is a fundamental reason underlying the exceptional on-stream reliability experienced in the commercial operations of the Wellman-Lord process.

The purge treatment section at NIPSCO selectively removes inactive oxidized sodium compounds from a sidestream of the absorbing solution and converts this material into a dry granular product which is marketed.

The third section of the Wellman-Lord process involves thermal regeneration of the absorbing solution to release the absorbed $SO_2$ as a concentrated gas stream and return of the reconstituted solution to the absorber.

The concentrated $SO_2$ gas may be converted to either elemental sulfur by Allied Chemical's $SO_2$ Reduction Process or to sulfuric acid by the Well-known contact process.

## Allied Chemical $SO_2$ Reduction to Sulfur

At NIPSCO, sulfur is recovered by Allied's $SO_2$ reduction process which consists of two principal operating sections.

In the primary reduction section, more than one-half the entering $SO_2$ is converted to elemental sulfur. A key feature of this section is the effective control of chemical reactions between $SO_2$ and natural gas over a low cost catalyst developed by Allied for this purpose. Heat generated by these chemical reactions is recovered and utilized to preheat the $SO_2$ gas stream entering this section.

Packed bed regenerative heaters provide a rugged and efficient means for achieving this heat exchange function. The process gas flow through the regenerators is periodically reversed to alternately store and remove heat from the packing; hence, the overall section is thermally self-sustaining.

Automatic control of the flow reversing cycles and other process conditions achieves optimum performance in the system, with high sulfur recovery efficiency and reductant utilization at all operating rates.

The secondary reaction section uses another catalyst which converts the remainder of the sulfur values in the process stream to elemental sulfur.

Sulfur produced in each section is removed from the process, stored and shipped as a hot liquid product.

After the sulfur has been removed, the gas stream is incinerated and returned to the Wellman-Lord absorber for recovery and recycle of the residual $SO_2$. There are no exits or effluents requiring separate disposal.

A flow diagram showing the combined Wellman-Lord/Allied Chemical processes is shown in Figure 1.

## SYSTEM PERFORMANCE AT NIPSCO

Results were better than the performance criteria established for the acceptance test period. The criteria and results obtained are detailed below.

### 92 MW Equivalent Test

### $SO_2$ Removal

1. Required: Minimum $SO_2$ removal of 90%, measured continuously and averaged every 2 hours.

2. Results: $SO_2$ removal averaged 91% over the 12-day test period. In only two 2-hour periods (out of 144) was the $SO_2$ removal less than 90%, and for those periods, it averaged 88% and 89%. Daily results are shown in Figure 2.

### Particulate Removal

1. Required: Particulate emission measured once daily will not exceed the Federsl NSPS for fossil fuel fired steam generators of 0.1 lb/million Btu heat input.

2. Results: Particulate emission averaged 0.04 lb/million Btu, or 40% of the maximum allowable. Of the 12 days, tests could not be run on four days due to inclement weather. On one day, the test data was not valid. Daily results are shown in Figure 2.

### Soda Ash Consumption

1. Required: Average over the 12-day test period not to exceed 6.6 STPD.

2. Results: Soda ash consumption determined by daily inventory obtained from storage bin measurement (official result) averaged 6.2 STPD, or 94% of the maximum allowable. Consumption determined by manually weighing the feeder output every two hours throughout the 12-day test period averaged 5.7 STPD, or 86% of the maximum allowable. Daily results are shown in Figure 2.

### Aggregate Cost of Steam, Electricity and Natural Gas

1. Required: Aggregate cost not to exceed $56 per hour based on predetermined unit cost.

2. Results: Hourly cost averaged $43 per hour over the 12-day test period, or 77% of the maximum allowable. Daily results are shown in Figure 2.

### Sulfur Purity

1. Required: Minimum sulfur purity 99.5%, suitable for conversion to quality sulfuric acid by standard production practice.

2. Results: Sulfur purity determined from a composite sample collected over the 12-day test period was 99.9%, easily exceeding the required purity.

## 110 MW Equivalent Test

### $SO_2$ Removal

1. Required: Minimum $SO_2$ removal of 90%, measured continuously and averaged every 2 hours.

2. Results: $SO_2$ removal averaged 91% over the 3-1/2 day test period. In only one 2-hour period (out of 42) was the $SO_2$ removal less than 90%, and for that period, it averaged 89%. Daily results are shown in Figure 3.

### Particulate Removal

1. Required: Particulate emission measured once daily will not exceed the Federal NSPS for fossil fuel fired steam generators of 0.1 lb/million Btu heat input.

2. Results: Particulate emission averaged 0.04 lb/million Btu, or 40% of the maximum allowable. Of the 3-1/2 days, a test could not be run on one day due to inclement weather. Daily results are shown in Figure 3.

## Viability of the Wellman-Lord FGD System

During the 12-day test period at the 92 MW equivalent rate, there was a total of 26 hours in interruptions in the fully integrated operation of the FGD system. Of the 26 hours, 18 were related to boiler problems and 8 were related to problems in the sulfur plant. In addition, there was a 4-hour period in which the $SO_2$ removal averaged "only" 88.5%; this 4-hour period was added to the acceptance test at the end of the 12-day test period. It should be mentioned that outages in the sulfur plant did not interrupt $SO_2$ removal. Furthermore, an $SO_2$ removal of

88.5% at the NIPSCO site falls well below an emission of 1.2 lb/million Btu heat input. During the acceptance test the parameters used by EPA for judging the viability of a FGD system were: availability, 94%; reliability, 100%; operability, 100%; utilization factor, 94%. Similar results are expected during the demonstration year.

## ECONOMICS

### Capital and Operating Costs

The estimated capital investment and operating costs of a Wellman-Lord FGD installation for a typical midwestern 500 MW power station burning 3% sulfur coal are shown in Tables 1 and 2. Both the elemental sulfur and sulfuric acid options are offered.

### Energy Requirements of the Wellman-Lord System

The Wellman-Lord $SO_2$ Recovery System has been portrayed by others as being a high energy user when compared to other FGD systems. However, it can be shown that this portrayal is not justified.

The Wellman-Lord FGD Process requires low pressure steam for regeneration of the absorbing solution. Turbine extraction or exhaust steam is ideally suited for the requirements. However, it is not always possible to modify the power plant cycle in order to provide this type steam, especially when the application is a retrofit.

In these cases, the steam required is provided directly from the steam drum after a suitable pressure reduction. Main steam provided to the Wellman-Lord System is arbitrarily assigned a cost equivalent to that of producing this steam in the power plant. This is a higher energy consumption than is actually incurred.

A typical modern power plant will operate with steam to the turbine at 2400 psi and 1000°F. The turbine exhaust will be at 2.5 in. Hg absolute, and the corresponding saturated condensate will be at a temperature of 109°F. After various reheat stages, the boiler feedwater will be at a temperature of about 475°F. The corresponding enthalpies of water at the various stages are:

| | | | |
|---|---|---|---|
| 1. | Boiler feedwater: | 459 Btu/lb | |
| 2. | Main steam: | 1462 Btu/lb | |
| 3. | Turbine exhaust steam: | 1020 Btu/lb | (75% efficient turbine) |
| 4. | Condensate: | 77 Btu/lb | |

Of the 1000 Btu/lb of energy provided to water in the boiler, only 440 Btu/lb - or 44% - is actually used in a turbine to produce electric power. The remainder - 56% - is rejected to the environment via a condenser and cooling tower!

Conversely, the Wellman-Lord FGD system will expand steam through turbine(s) driving the booster blower(s) to greatly reduce electric power consumption. The energy remaining in the turbine exhaust steam will then be utilized to regenerate the absorbing solution. Furthermore, uncontaminated condensate will be returned to the power plant at or near its normal boiling point, thereby reducing the amount of energy required to heat the water back up to the normal boiler feed temperature.

The steam cost charged to the Wellman-Lord system should, therefore, be corrected by a factor corresponding to the much more efficient utilization of energy. Furthermore, credit should be given the Wellman-Lord system for the return of hot, uncontaminated condensate.

Purely from an energy standpoint, about 7 lb/hr of main steam are required to produce 1 kw of electric power in a modern power plant. In a Wellman-Lord FGD system applied to a 500 MW power plant burning 3% sulfur coal, about 200,000 lb/hr of steam will be required for absorbing solution regeneration. This amount of steam is equivalent to about 28.6 MW of electric power generation. In addition, 5000 HP - or 3.4 MW - are required for the Wellman-Lord system in question.

The total energy consumption of the Wellman-Lord system then is 32.0 MW, or 6.4% of the generated power. Recent applications of lime/limestone FGD systems show energy requirements of the same order.[1]

## WELLMAN-LORD VS. THROWAWAY

Why should a utility select the Wellman-Lord FGD system instead of a throwaway system? There are several reasons for making this decision.

### Cost

It has been previously reported that a Wellman-Lord FGD system requires more capital investment than a throwaway system. This difference is rapidly becoming non-existent. In order to ensure reliability, throwaway processes are becoming more expensive. Furthermore, when the cost of waste sludge disposal is added to the cost of the FGD system, throwaway processes often become more expensive than Wellman-Lord.

### Reliability

While the reliability of lime/limestone scrubbing systems has shown some improvement, one basic fact about these systems remains unchanged. As $SO_2$ is absorbed into the scrubbing medium, the latter becomes more insoluble. Small departures from narrow operating margins usually result in scaling and/or plugging in the absorber with consequent downtime. After ten months of operation at NIPSCO, the historical performance of the Wellman-Lord system remains unchanged. A Wellman-Lord absorber has never been shut down due to scaling and/or plugging. Furthermore, it requires little operator attention.

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[1] Forsythe, R. C., "Experiences with Flue Gas Desulfurization at the Bruce Mansfield Plant," Conference on Coal Gasification, Liquefaction and Conversion to Electricity, Pittsburgh, August 1977.

### Waste Disposal

Sulfuric acid or elemental sulfur are useful products that can be marketed. Large quantities of sulfuric acid are used in the chemical, agricultural and oil industries. Elemental sulfur is used primarily in the manufacture of sulfuric acid. Sulfuric acid or elemental sulfur users will pay a competitive price for the product from a Wellman-Lord FGD system. This will partially offset the cost of flue gas desulfurization via Wellman-Lord.

The sulfate purge from a Wellman-Lord system can be marketed. Sodium sulfate is also a byproduct of the rayon fiber industry. However, the amount of sodium sulfate available from this source is declining and will continue to do so in the foreseeable future. The pulp and paper industry has - and will continue to have - a demand for sodium sulfate. DPG believes that marketing of this commodity is by no means an impossible task.

Conversely, at present there is no market for the sludge produced by a throwaway system, and the economic and environmental impacts of a sludge disposal system are uncertain. These have been described recently.[1]

## QUALIFICATIONS FOR FUTURE PROJECTS

### Davy Powergas

The experience of Davy Powergas in $SO_2$ recovery began with the start-up in 1970 of the first Wellman-Lord installation. Development work by Davy on predecessor processes dates back to 1965. Since 1970, 25 installations have been completed and are in regular commercial service, and five more are in various stages of engineering and construction.

While the NIPSCO project represents the first application of Wellman-Lord technology to a coal-fired utility boiler, pilot plant tests made prior to design work indicated that no major difficulties were to be expected in applying the process to coal-fired boilers. This expectation has been confirmed in operations at NIPSCO to date. Construction of Wellman-Lord FGD facilities for two 350 MW coal-fired units will be completed early in 1978, and an installation on a 550 MW boiler is in the early construction stages.

The Wellman-Lord process offers more experience in commercial service than any other regenerable system. Its operating reliability, flexibility, and $SO_2$ removal efficiency are well proven, and the fact that a valuable resource is recovered rather than creating a waste product should make the system more attractive to many power plants.

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[1] Forsyhte, R. C., "Experiences with Flue Gas Desulfurization at the Bruce Mansfield Plant," Conference on Coal Gasification, Liquefaction and Conversion to Electricity, Pittsburgh, August 1977.

Davy Powergas offers this long experience in regenerable FGD systems in the form of process and design engineering, procurement services, full construction services, and start-up assistance.

## Allied Chemical

Allied Chemical is one of the largest producers of sulfuric acid for the merchant market and consumes more than 700,000 tons of sulfur each year.

Today, eight of Allied's fifteen North American sulfuric acid locations can reprocess sulfur-containing waste material from petroleum refineries, detergents manufacturers and other industries. Allied Chemical's participation in the FGD project at Mitchell Station is a logical extension of sulfur pollution control services provided to others for many years. Many companies not experienced in chemical operations and chemical markets call upon Allied to provide specialized technology and/or services in the recovery of sulfur values from polluting wastes.

Allied Chemical is prepared to provide to electric utilities a full range of technical, operating, maintenance and marketing services necessary for the long-term implementation of a sound regenerable FGD program yielding either sulfur or sulfuric acid as the principal useful product. Allied Chemical is prepared to manage a regenerable FGD facility as it would its own chemical plants and bring to bear on-site experience and in-depth support of a national sulfur products network to assure successful execution.

## CONCLUSION

There is every expectation that the NIPSCO regenerable FGD installation will continue to demonstrate the efficiency and reliability sought by the electric utility industry for the control of $SO_2$ emissions from coal fired boilers.

The management of NIPSCO with the encouragement and assistance of the EPA took a progressive and forward looking step in their decision to proveed with this regenerable FGD project. Transformation of $SO_2$ in flue gas to useful chemical products rather than worthless sludge is an objective worthy of serious consideration by the power industry.

Concentrated $SO_2$ from the Wellman-Lord $SO_2$ Recovery Process may be converted to either sulfur or sulfuric acid.

Davy Powergas is prepared to design and build a FGD system to recover sulfur or sulfuric acid from the flue gas of any size fossil fuel fired boiler in the power industry.

Allied Chemical is prepared to operate such a regenerable FGD facility for the electric utility producing either useful product and is prepared to undertake marketing arrangements to assure long-term distribution of either sulfuric acid or sulfur.

### TABLE 1

### NOVEMBER 1977 COST PROJECTION
### WELLMAN-LORD FGD PROCESS
### SULFURIC ACID RECOVERY

| | |
|---|---|
| BASIS: | 500 MW Coal Fired Power Plant<br>Midwestern 3% Sulfur Coal, 10,600 Btu/lb<br>Capacity Factor - 80%<br>Fourth Quarter 1977 U.S. Dollars |

| | |
|---|---|
| INSTALLED CAPITAL COST BATTERY LIMITS: | $35,500,000 |
| ANNUAL OPERATING COSTS: | $1,000 |
| Soda Ash ($89/ton dlvd. Midwest) | 910 |
| Steam ($1.30/1000 lbs.) | 1,820 |
| Cooling Water ($0.01/1000 gal.) | 80 |
| Process Water ($0.05/1000 gal.) | 10 |
| Electricity (15 mills/kwh) | 530 |
| Adm. & Supervision $14/hr incl. fringes) | 170 |
| Operating Labor ($10/hr incl. fringes) | 390 |
| Overhead (75% of labor & supervision) | 420 |
| Maintenance (3.5% of capital) | 1,220 |
| Total Direct Operating Expense | 5,550 |
| Credit from Sale of Acid ($15/ton) | (1,660) |
| Net Direct Operating Expense | 3,890 |
| Capital Charges (18% per year) | 6,300 |
| TOTAL | 10,190 |

Capital Cost = $71/kw
Annual Operating Cost = 2.9 mills/kwh

## TABLE 2

## NOVEMBER 1977 COST PROJECTION
## WELLMAN-LORD FGD PROCESS
## WITH SULFUR RECOVERY BY
## ALLIED CHEMICAL $SO_2$ REDUCTION PROCESS

BASIS:
500 MW Coal Fired Power Plant
Midwestern 3% Sulfur Coal, 10,600 Btu/lb
Capacity Factor - 80%
Fourth Quarter 1977 U.S. Dollars

| | |
|---|---|
| INSTALLED CAPITAL COST BATTERY LIMITS: | $37,500,000 |
| ANNUAL OPERATING COSTS: | $1,000 |
| Soda Ash ($89/ton dlvd. Midwest) | 910 |
| Natural Gas ($2.00/MCF) | 970 |
| Steam ($1.30/1000 lbs.) | 1,820 |
| Cooling Water ($0.01/1000 gal.) | 60 |
| Process Water ($0.05/1000 gal.) | 10 |
| Electricity (15 mills/kwh) | 530 |
| Adm. & Supervision ($14/hr incl. fringes) | 170 |
| Operating Labor ($10/hr incl. fringes) | 390 |
| Overhead (75% of labor & supervision) | 420 |
| Maintenance (3.5% of capital) | 1,310 |
| Total Direct Operating Expense | 6,590 |
| Credit from Sale of Sulfur ($40/long ton) | (1,300) |
| Net Direct Operating Expense | 5,290 |
| Capital Charges (18% per year) | 6,750 |
| TOTAL | 12,040 |

Capital Cost = $75/kw
Annual Operating Cost = 3.4 mills/kwh

FIGURE 1

WELLMAN - LORD $SO_2$ RECOVERY/ALLIED CHEMICAL REDUCTION TO SULFUR

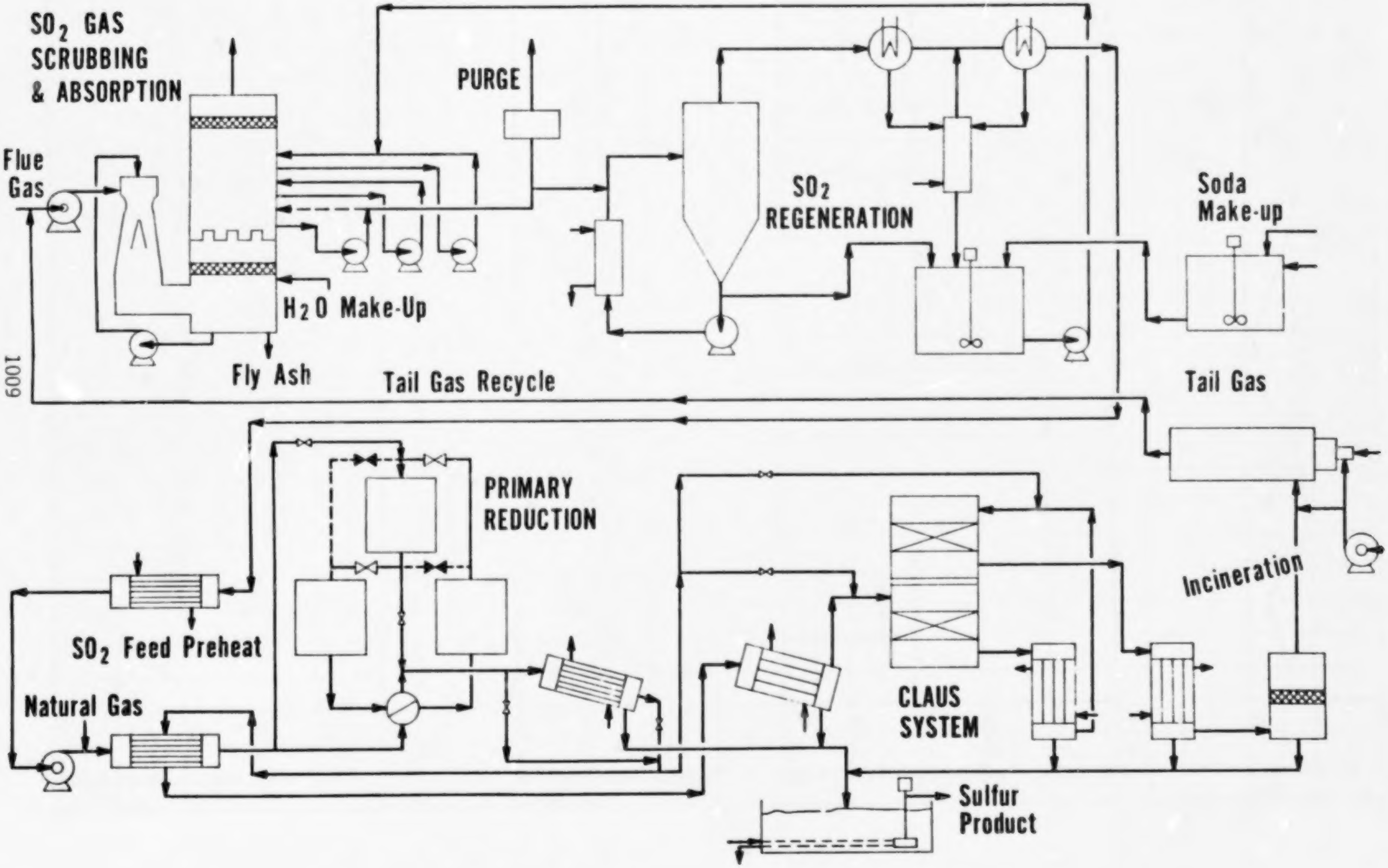


Figure 2 - 92 MW Performance Test Parameters

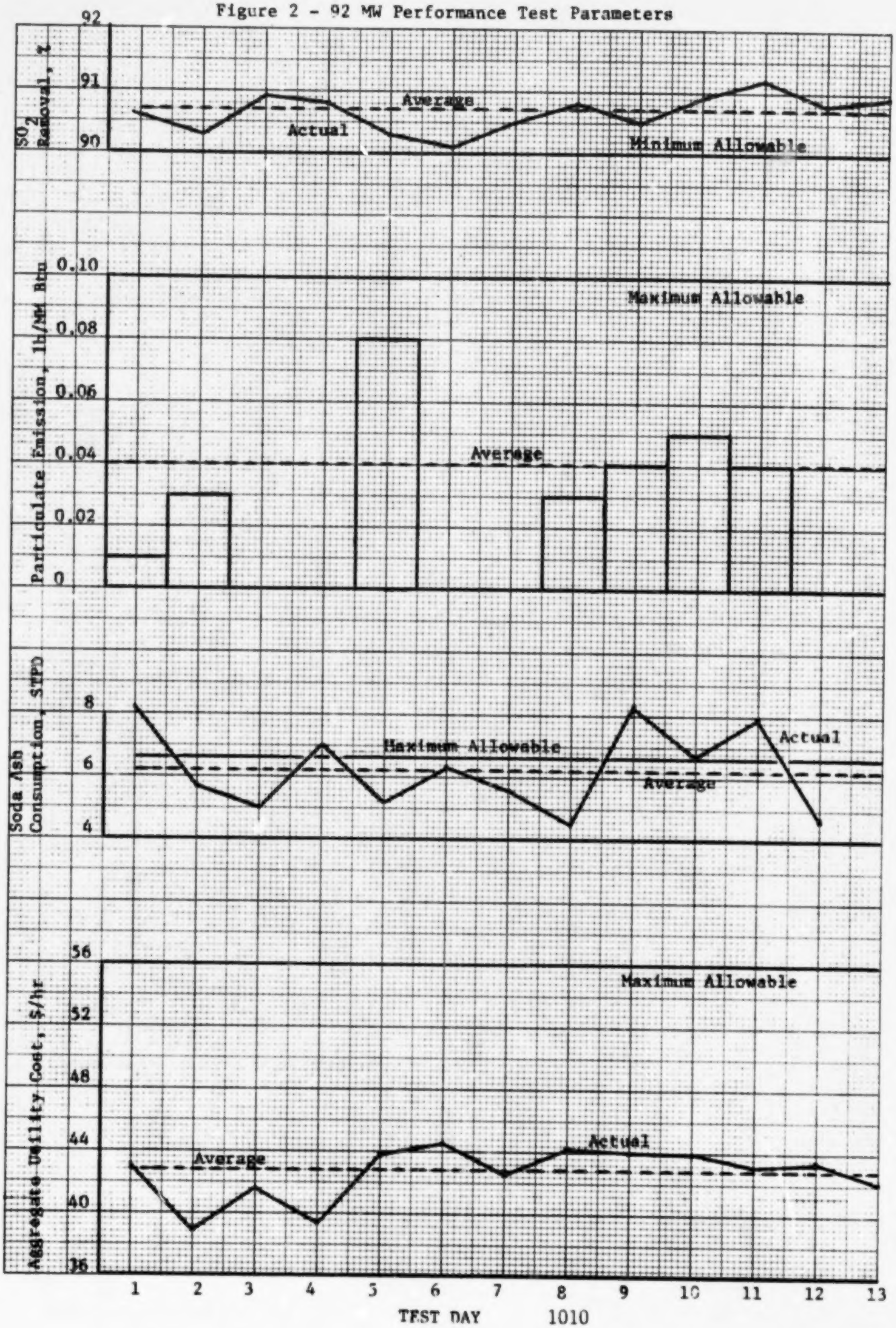
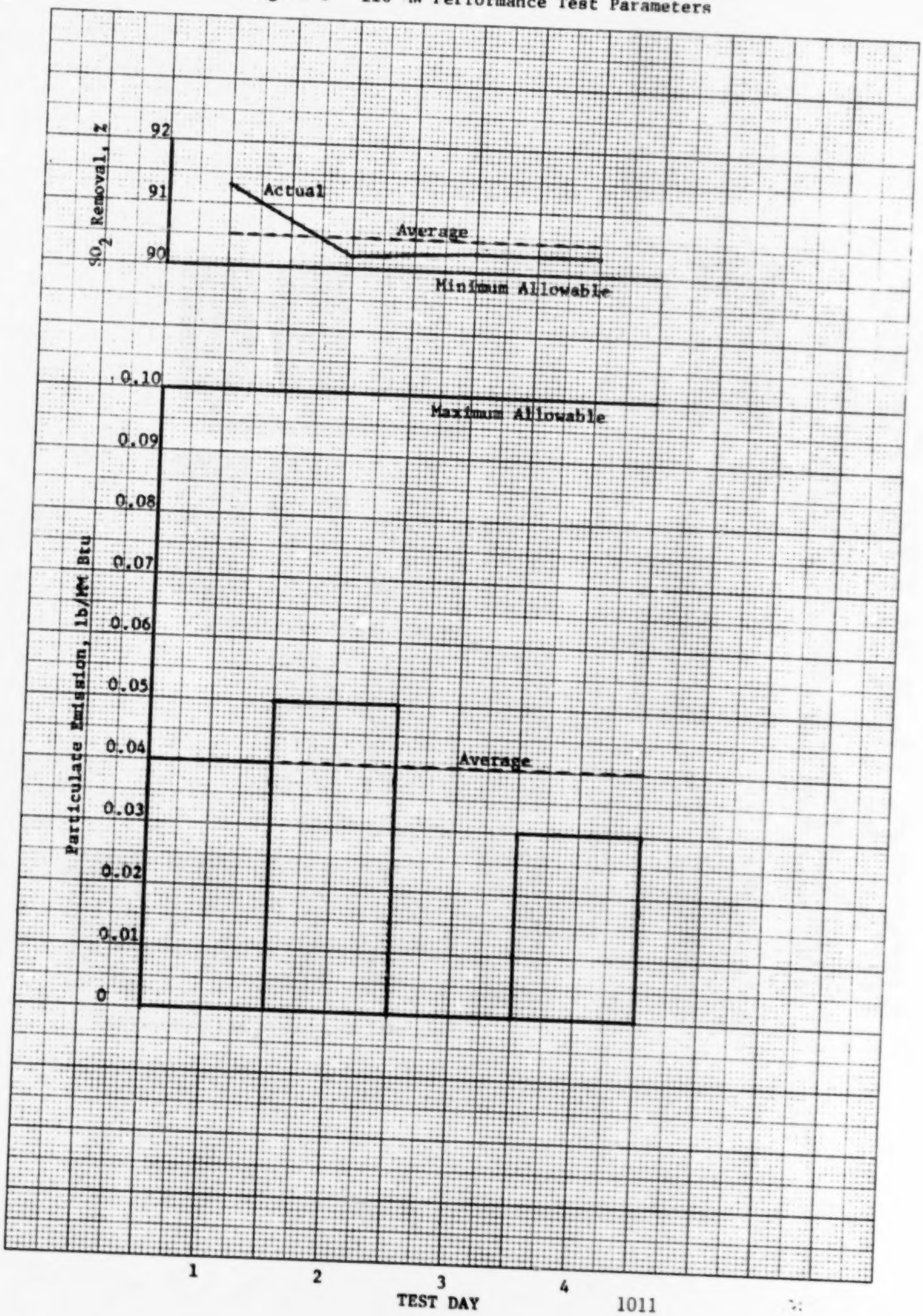


Figure 3 - 110 MW Performance Test Parameters



"EXHIBIT 1"

# NIPSCO-Unit 11 FGD Facility Allied Chemical Functions

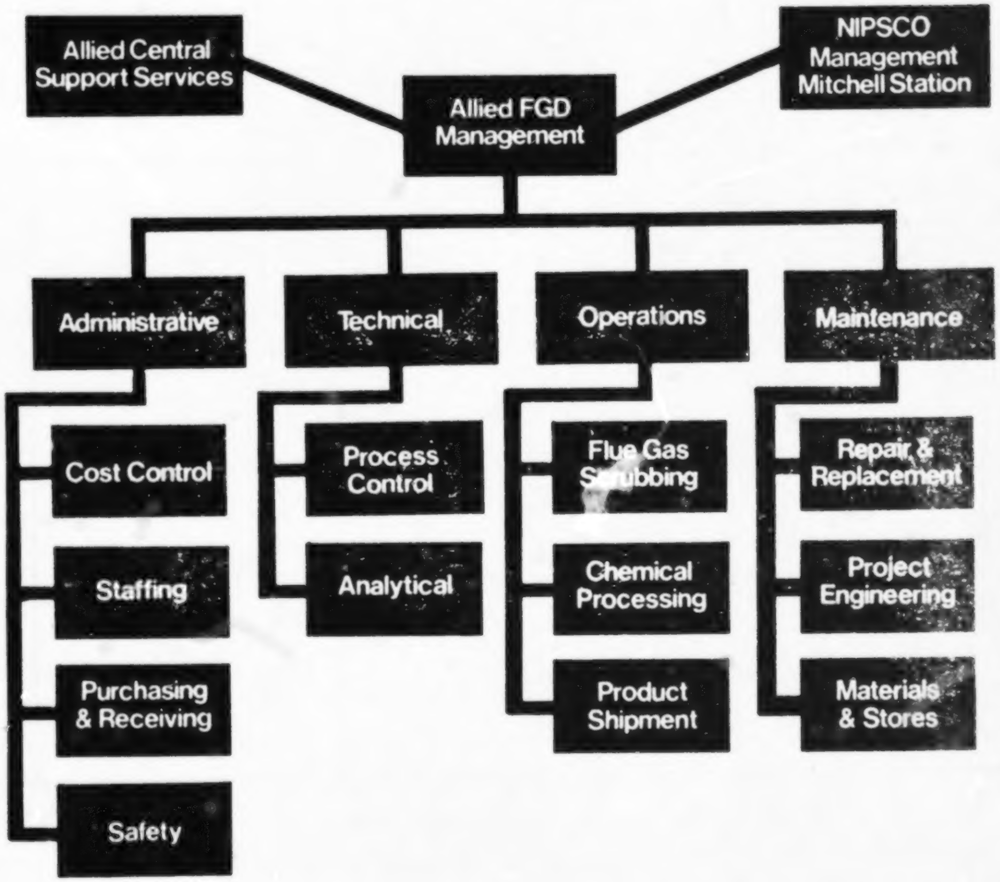


EXHIBIT 2

# NIPSCO EMISSION CONTROL SYSTEM

## Start - Up and Performance Testing

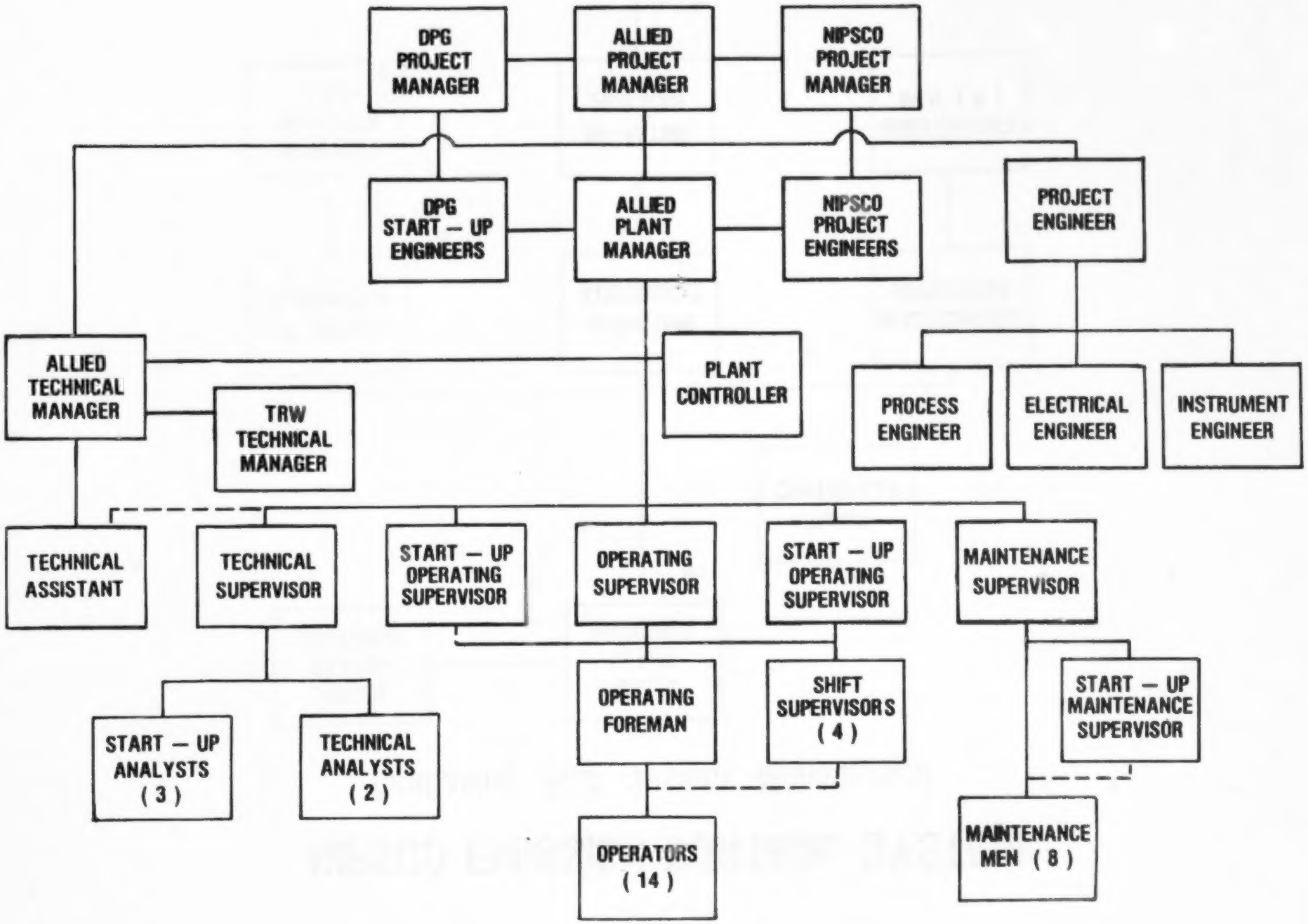


EXHIBIT 3

# NIPSCO EMISSION CONTROL SYSTEM

## Continuing FGD System Management

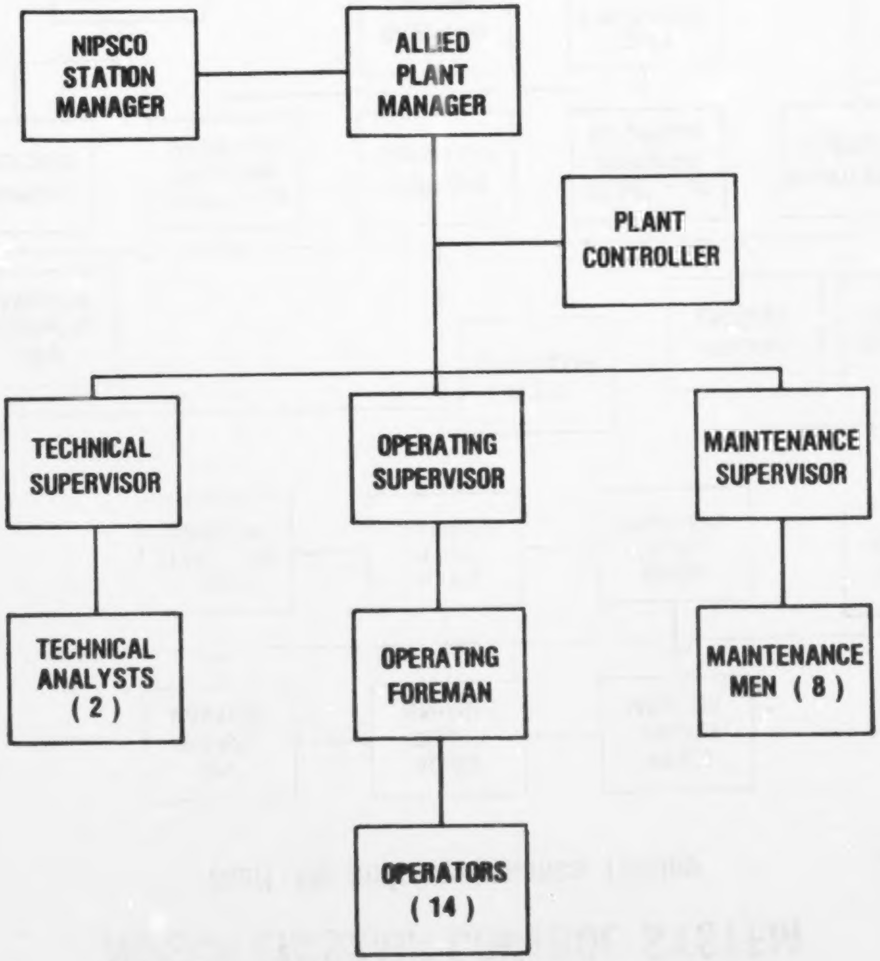
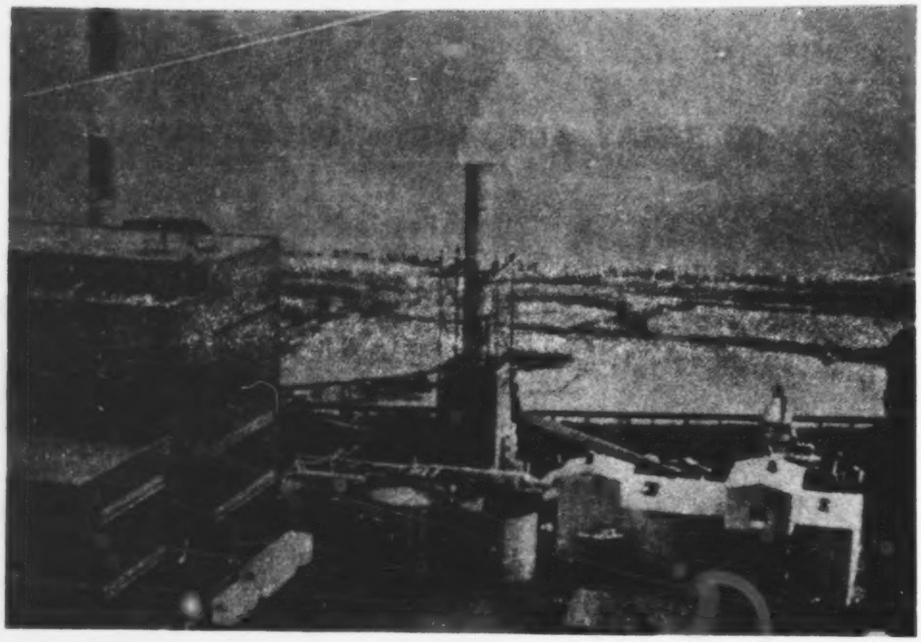
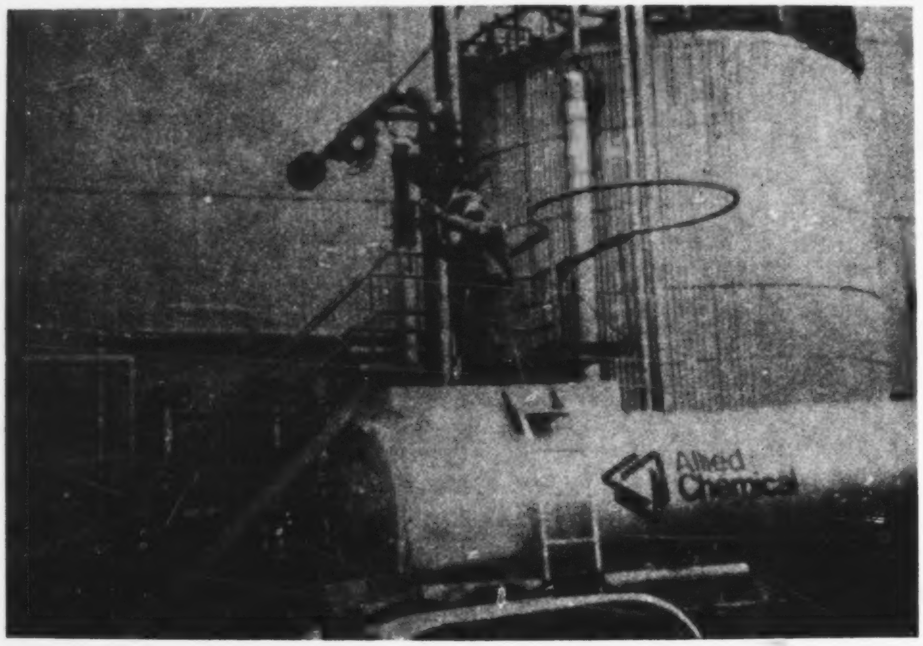


Exhibit 4



Regenerable FGD Facility Next to NIPSCO's Mitchell Station



Loading Sulfur Recovered from the $SO_2$ Emission Control Facility at NIPSCO's Mitchell Station

# $SO_2$ SPRAY ABSORPTION WITH DRY WASTES

**K. Felsvang,**
**K. Gude,**
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Niro Atomizer, Inc.
Columbia, Maryland

# $SO_2$ SPRAY ABSORPTION WITH DRY WASTES

by

K. Felsvang
K. Gude
S. Kaplan

NIRO ATOMIZER

Technology which has been used within the field of industrial spray drying for more than forty years has now been adapted for solving the problems associated with flue gas desulfurization.

The Niro Atomizer spray absorption system is designed for $SO_2$ removal from boiler exhaust gases. It can further be utilized for removal of HCL or other harmful gases. The process, which is very similar to conventional spray drying technology, is outlined in Figure 1. It consists of the feed preparation system, which will vary depending upon the absorbant to be utilized, a transportation system for delivering the feed from the preparation site to the atomization assembly, a rotary or spinning wheel atomizer for absorbant atomization in the process chamber and a gas distribution system for obtaining the correct gas-liquid mixing within the chamber. This, along with the dust collection equipment, will remove all sulfur oxide and particulate pollutants prior to the flue gas emission into the atmosphere and will produce a dry residue which can be disposed of along with fly ash wastes, thereby requiring no further treatment.

The preparation system for the absorbing slurry must be designed very carefully, and varying conditions during the mixing stages can have substantial effects on the absorbant utilization. Extensive test work has shown that in the case of lime, for instance, the type of quick lime used and the method of mixing it with water can effect $SO_2$ removal efficiencies significantly. By selecting optimum operating conditions, up to 90% $SO_2$ removal has been achieved. Other materials, such as sodium carbonate based minerals, have not shown as drastic variations due to preparation parameters, but close control must be maintained nevertheless to assure that the proper concentration of solids necessary for the desired $SO_2$ removal will be present.

The transportation system for delivering the absorbant will consist simply of a pump capable of moving a high solids' slurry. With the Niro Atomizer rotary atomizer, there are no pressure requirements at which the feed must enter the wheel; therefore, the feed will be pumped to a small constant pressure head tank on the top of the reaction chamber and will then flow to the atomizer by gravity. By utilizing this set-up, all high pressure components have been eliminated completely as simple centrifugal pumps will be utilized for slurry delivery.

The key to the entire system is the atomization of the absorbing slurry and the intermixing of this atomized slurry with the boiler exhaust gases. Niro Atomizer is capable of supplying single rotary atomizers which can handle up to 200 metric tons per hour of slurry when required. Systems to treat up to 500,000 ACFM in a single chamber have been designed where absorbant feed rates in the order of 20 to 35 metric tons per hour are fed. With the larger atomizer capability, higher gas flow rates per chamber are possible. The absorbant is atomized by the forces exerted on it as it is thrown from the spinning disk or wheel. The wheel contains up to 24 orifices, about one-half inch in diameter, and as the slurry is accelerated through the internal section of the wheel, it is thrown out through these orifices, breaking into millions of small droplets. This special patented abrasion resistant wheel is currently used throughout the world for atomizing highly abrasive slurries such as in mineral concentrates, cement and kaolin. The speed of the wheel can be in the order of ten thousand revolutions per minute and by changing this speed, the size of the droplets produced can be modified. As the droplets exit from the wheel, a cloud is formed which extends horizontally throughout much of the chamber (See Figure 2).

It is critical that the droplets in this cloud mix completely with incoming boiler flue gases to achieve the necessary $SO_2$ removal, and equally important to have complete water evaporation take place before the slurry droplets come in contact with the chamber wall.

Optimum mixing is achieved by means of the flue gas distribution system shown on Figure 2. The flue gas leaves the air preheater and is transported to a roof gas disperser which funnels the gas evenly around the atomizer as it enters the chamber. A series of adjustable vanes in the gas disperser give the gas a swirling motion to provide for complete interaction of the $SO_2$ laden gas with the atomized absorbing droplets.

As this interaction occurs, the $SO_2$ in the gas reacts with the active material in the atomized slurry while at the same time water is evaporated to form a dry product. Part of this dried powder can then be collected in the absorption chamber which, through its design, acts as a cyclone separator, or the powder can be collected in the same dust collection equipment used for fly ash removal. It is possible to split the percentage of dust collected in the absorber and precipitator or baghouse so that by collecting a larger quantity in the absorber, the requirements of the dust collection equipment down stream can be reduced significantly.

Temperatures within the absorption system are closely controlled, as in normal spray dryer operation. The outlet temperature is held enough above the dew point to allow for a temperature drop across the dust collection equipment without causing any operational problems. This is especially important when a baghouse, which is sensitive to both high and low temperatures, is used. Since the temperature at the absorber outlet can be controlled to within two degrees, it is possible to utilize low temperature bag materials within the baghouse which could reduce both capital and operational costs.

Keeping a close temperature control over the system is also important when considering that the amount of active material to be utilized will vary as inlet $SO_2$ concentrations vary. Test work has indicated that stoichiometric ratios approaching those achieved in conventional wet scrubbers can be obtained. It is, therefore, important to maintain a very tight control over temperature, from a material consumption viewpoint as well as to avoid operational problems.

Whereas in a wet scrubbing process the wet sludges represent a major pollution problem in themselves, the residue from the dry absorption system is a dried, free-flowing powder which can be disposed of in a manner similar to normal fly ash disposal. It will not be necessary to provide any further treatment to these wastes and the volume of material which must be disposed of is substantially less than that produced by a wet scrubber. Also, since there is no further treatment of the wastes, equipment such as thickeners, centrifuges, and filters can be eliminated, which will greatly reduce the amount of land necessary for a pollution control system.

From a maintenance point of view, the dry $SO_2$ absorption process offers many advantages over conventional wet scrubbing systems. Since there is no wet-dry interface, problems usually occurring, such as scaling within the scrubber, have been eliminated. Also, since the feed transportation system is simpler in the dry process, the likeliness of mechanical problems in transporting the absorbant is reduced. And, as already discussed, the removal of the dry residue from the absorber presents no problems while sludge from a wet process will result in material handling as well as disposal problems.

The Niro Atomizer spray absorption system offers a new method for removal of $SO_2$ from boiler off gases while employing concepts and operations which have been used in conventional spray drying plants for over forty years. High tonnage spray dryers have consistently shown the high reliability and continuous service which is essential for operation in the utility industry. It is, therefore, possible to eliminate the problems with existing flue gas desulfurization systems by utilizing this unique spray absorption process with dry waste disposal.

Figure 1

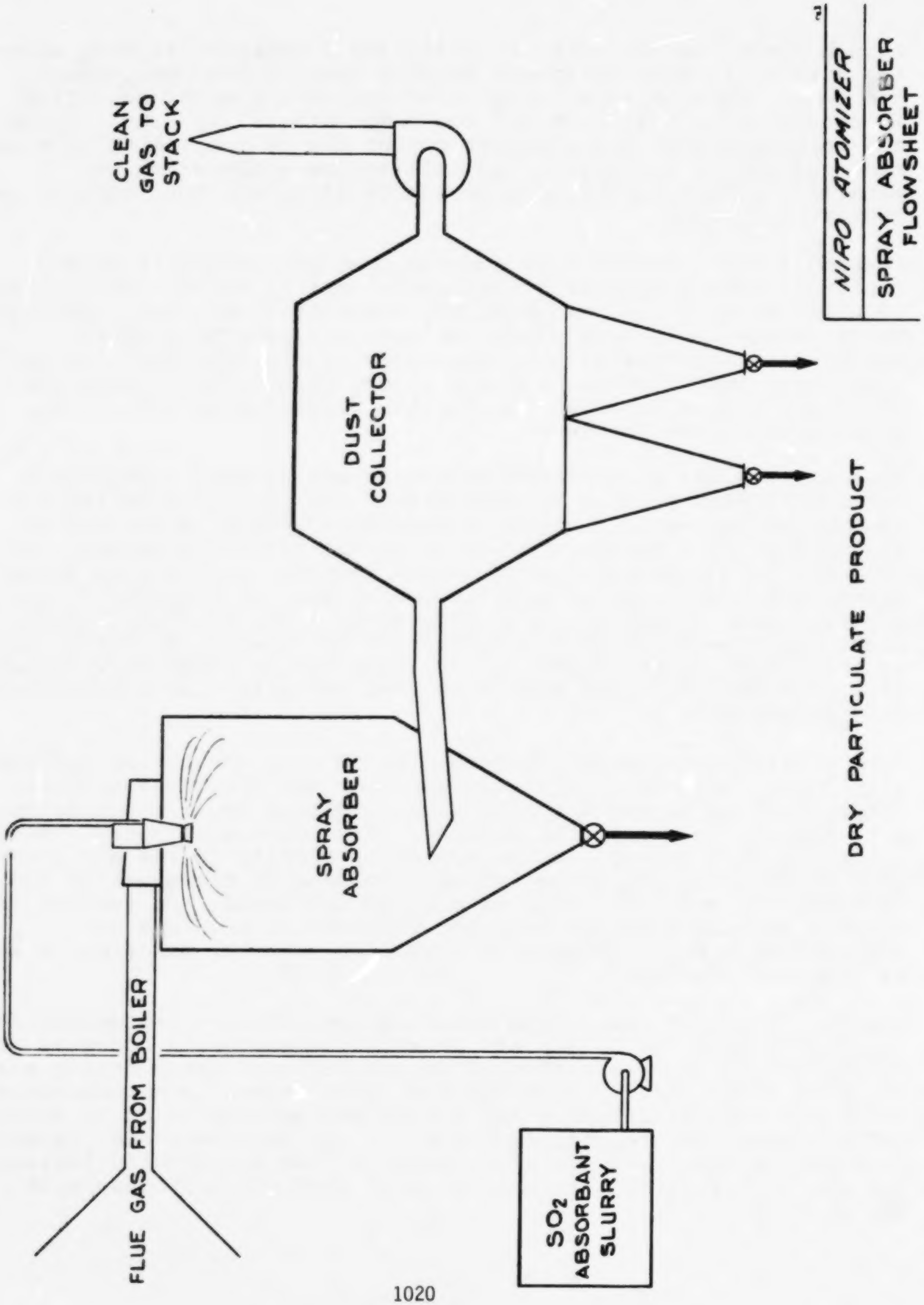
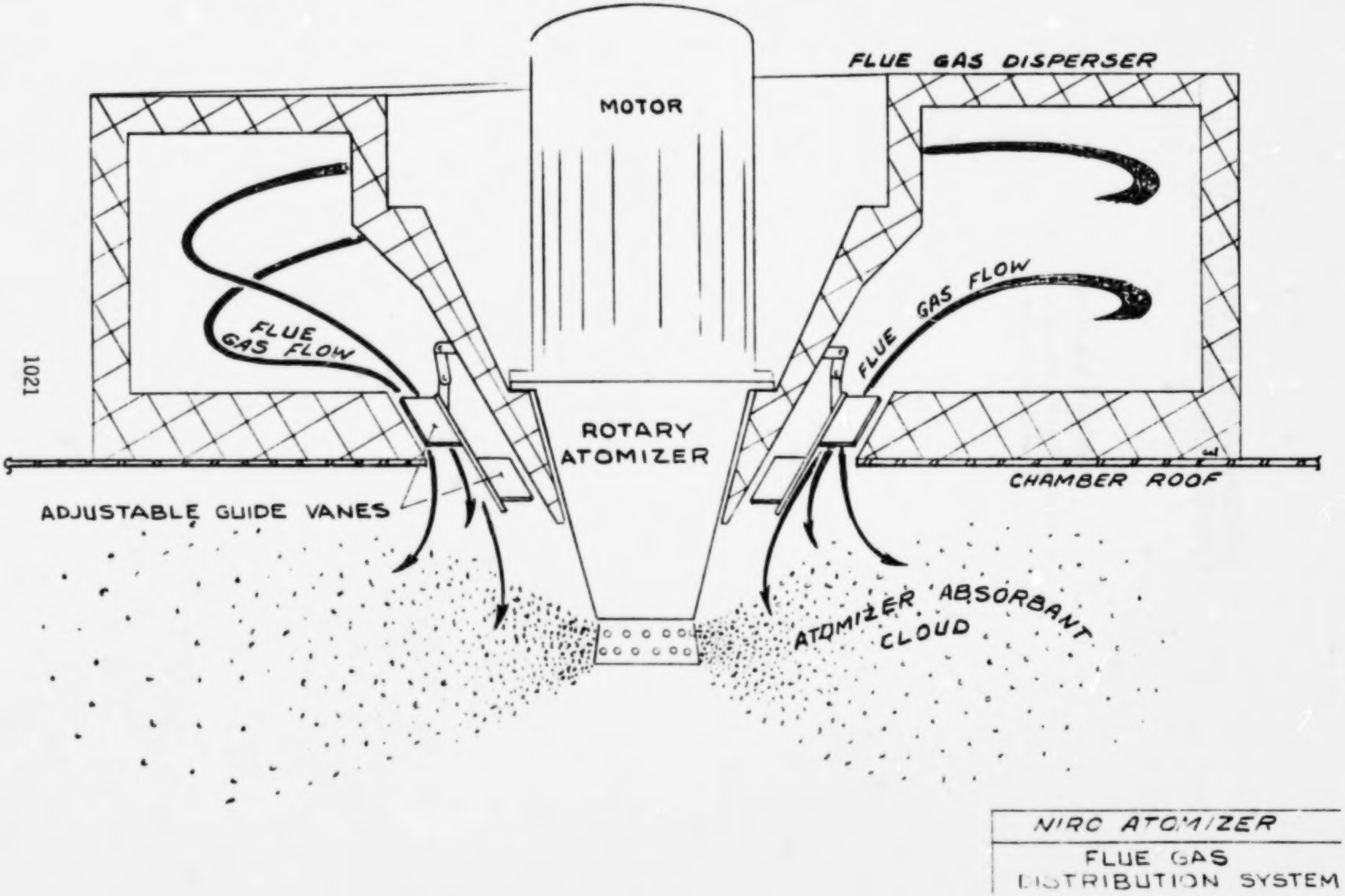

CLEAN GAS TO STACK
DUST COLLECTOR
SPRAY ABSORBER
DRY PARTICULATE PRODUCT
FLUE GAS FROM BOILER
$SO_2$ ABSORBANT SLURRY
NIRO ATOMIZER
SPRAY ABSORBER FLOWSHEET

Figure 2


FLUE GAS DISPERSER
MOTOR
FLUE GAS FLOW
FLUE GAS FLOW
ROTARY ATOMIZER
CHAMBER ROOF
ADJUSTABLE GUIDE VANES
ATOMIZER ABSORBANT CLOUD
NIRO ATOMIZER
FLUE GAS DISTRIBUTION SYSTEM

# CIRCUMSTANCES OF FGD AT CHUBU ELECTRIC POWER CO.

**Masato Miyajima**
Chubu Electric Power Co., Ltd.
Nagoya, Japan

# Circumstances of FGD at Chubu Electric Power Co.

Masato Miyajima
Chubu Electric Power Co., Ltd.
Nagoya, Japan

In Japan, where its national territory, particulary the inhabitable area is quite limited, both population and industry are much too overcrowded.

For this reason, residential districts are not quite separated from industrial districts, and in the past we experienced problems where atmospheric pollution had resulted in damages to the health of the inhabitants.

In the city of Yokkaichi, in spite of the fact that six factories including our power plant were operating by abiding by the emission standards respectively, we were sued for the alleged damages to the health of the local inhabitants owing to the exhaust gas, and the trials have resulted to impose exceedingly severe control on us, the enterprises.

In Japan, as regards emission of SOx, in accordance with the agreement concluded with the local governments, it is strictly specified to be equivalent of 0.1 to 0.3 percent in terms of sulphur content. Since long before the problem of such atmospheric pollution came to the fore (the first half of the 1960s), this company has been studying problems relative to air pollution.

It is an opinion of the electric power suppliers as the users of the fuel that efforts towards supply of oil with less sulphur content should be made on the part of petroleum companies, suppliers of the fuel. However, in consideration of the demand-supply situation of low-sulphur crude oil, available technology for oil desulphurization, the capacity of existing necessary facilities and other reasons, it has become necessary to adopt the method of desulphurizing the flue gas. For such reasons that heavy oil with low sulphur content be used with priority for boilers operated by medium and small-size companies, some of the boilers belonging to power supply companies have been equipped with flue gas desulphurizing systems so as to cooperate in meeting the low sulphurization plan target which is being sought throughout the country.

The first process of desulphurization ever to be adopted by Chubu Electric Power Co. was the dry activated manganese oxide process. Based on this process, various test plants on different scales were constructed at our Yokkaichi Thermal Power Station as follows:

DAP - 3,000 (capacity 3,000 $Nm^3/hr$)
DAP - 55 (capacity 55 MW)
DAP - 110 (capacity 110 MW, (220 MW x 1/2))
(Note - DAP: dry absorption process)

Through researches conducted from 1964 to 1974, a large number of important data were obtained. This process, however, because of its own characterristics, failed to match the situation being prevalent then, and therefore no additional expansion of the process was effected.

In parallel with the dry process, this company was proceeding with research on wet processes, and having a prospect that the wet process is commercializable earlier than the dry process, as the first step, FGD of the Wellman-Lord process'on full scale was erected as No. 1 power plant (220 MW) at Nishi-Nagoya in September 1973.

The Wellman-Lord process was selected for the following reasons:

1) The quantity of raw materials required and the quantity of by-products turned out are small.

2) No possibility of scaling in the absorption tower unlike in the case of the lime gypsum process.

3) Japan Synthetic Rubber Co. has constructed one with a capacity: 100,000 $Nm^3/hr$.

4) The by-products $H_2SO_4$ is effectively usables as a chemical industry raw material. Further, it finds a rather large market and consequently problem is limited as to its disposal.

Operation results of the Wellman-Lord process at the Nishi-Nagoya Power Station during the past four years are as follows:

Operation time: 26,000 hours (Sept. 1973 - Sept. 1977)

Operation rate: 91%

Efficiency: $SO_2$ at inlet: 1,500 ppm

(equivalent to 2.5% sulphur content.)

$SO_2$ at outlet: 110 ppm

(equivalent to 0.2% sulphur content)

Mean desulphurization rate 92%

By-produced sulphuric acid: 60,200 tons

Principal troubles experienced and counter measures taken therefor:

(1) Clogging of fine pipes of the heater of the regeneration system evaporation boiler

Clogging and corrosion of the fine pipes of the heater due to depositing of such substances as sodium sulphite, and Glauber's salt. To eliminate the trouble, periodical washing with water (once monthly) and jet cleaning ( 3 to 4 times annually) are being conducted.

(2) Cracking in the interior of the absorption tower

Cracking was observed in the tray inside the absorption tower during the initial period following the startup.

As countermeasure, various parts were reinforced and as the result no similar troubles have occurred thereafter.

(3) Leak through the fine pipes of the surface condenser

Leak took place resulting from corrosion of the interior of the fine pipes (seawater side). As the solution, the material of the fine pipes was changed from stainless steel ( epoxy lined) to titanium.

We are almost content with the results obtained.

At No.1 and No.2 plants at the Owase Mita Power Station (with a capacity of 375 MW respectively), FGD of the lime gypsum process for total flue gas treatment was erected in the beginning of 1976.

The lime gypsum process was adopted for the reasons to be enumerated in the following:

1) This process, that has already been employed by other power supply companies, is now offering higher reliability.
2) The process itself is simple.
3) The raw material of lime is abundantly available in Japan.
4) Even in case where a large number of FGDs are set up in Japan in the future with resultant oversupply of the by-product of gypsum, it will be easy, unlike sulphuric acid, to store and discard in some cases, because of its chemical stability. What is more, gypsum is being consumed in large quantities for such purposes as making cement and gypsum boards, and it offers greater possibility of new applications and uses in the future.

Stepped up efforts are being made in that direction too.

Operation results of the lime gypsum process at the Owashe Mita Power Station are:

Operation time: No.1 11,000 hrs (April 1976-Sept. 1977)
No.2 9,600 hrs (June 1976-Sept. 1977)

Operation rate: No.1 96 %
No.2 99 %

Efficiency: $SO_2$ at inlet - 1,600 ppm
(equivalent to 2.9 % sulphur content),
$SO_2$ at outlet - 120 ppm
(equivalent to 0.25 % sulphur content),
mean desulphurization rate 92 %

Fuel consumption: No.1 860,000kl
No.2 760,000kl

Gypsum production: No.1 128,000 tons
No.2 133,000 tons

Principal troubles and countermeasures therefor:

(1) Clogging of the mist eliminator

There were instances where the trains were stopped alternately to be cleaned in turns because the differential pressure tended to increase owing to gypsum scale that deposited on the elements of the mist eliminator during the initial period following the startup.

(2) Slurry piping

Leakage through the slurry piping and valves due to local abrasion was detected particularly in the parts that were subjected to high temperature. Thus, the pipeline was modified in order to facilitate maintenance.

(3) Absorbing tower

Although partial clogging of the internal grid was seen, it did not lead to malfunction in particular. Cleaning of the grid was performed once annually at the time of periodical inspection.

(4) While clogging of the filter element of the gypsum separator (centrifugal machine) occurred frequently during the initial period following the startup, its occurrence was brought to a minimum by employing filter element of a different type and changing the operation method.

We are virtually satisfied with the foregoing results.

Re economics

Although the economics of desulphurization of flue gas that are related to the operations of this company cannot be stated definitely, they register at 6,000 to 8,000 yen per kl by a 7-year depreciation and a 70 % operation rate, and this is nearly equivalent to the fuel cost difference in Japan between high-sulphur oil and low-sulphur oil.

FGD in Japan, however, is of very high efficiency, including its after-treatment system in consideration of the various strict environmental standards, with resultant high costs, but in cases where very high efficiency is not called for depending on the sitting conditions of power plants, the cost is expected to be somewhat lower.

On the other hand, in Japan although primary emphasis used to be placed on SOx in the past by way of environmental control of thermal power stations, the control standards are becoming increasingly severer of late extending over to all areas such as NOx, smoke dust, water quality and wastes, and FGD, too, in consideration of such control standards, has come to be placed in a delicate situation. In other words, use of HS consequent upon installation of the FGD entails increase in NOx generated, and as measures to be taken therefor more sophisticated techniques and greater costs are required. Use of the FGD, furthermore, incurs other problems which are associated with wastewater treatment and disposal of by-products.

In view of the above-mentioned background of the FGD, use of fuel with higher quality as well as use of fuels of diversified types and kinds, even LNG and naphtha have come to be employed. What is more, FGD has rarely been installed recently because the citing conditions of thermal power stations call for use of ultra low sulphur fuel (such as LNG and equivalent of naphtha) and flue gas with minimum NOx content. However, two units of coal-burning 500 MW FGDs are said to be installed at the Matsushima Power Station of the Electric Power Development Company which is scheduled to be completed in 1980.

# FLUE GAS DESULPHURIZATION PLANT ON OWASE-MITA POWER STATION

**Masato Miyajima**
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Nagoya, Japan

# FLUE GAS DESULPHURIZATION PLANT
# ON OWASE-MITA POWER STATION

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## Introduction

Owase-Mita Power Station's No.1 and 2 machines having a total output of 750,000 kW (375,000 kW x 2 units) was started in operation in July and September, 1964, respectively.

Since then we have made a maximum effort in lowering the sulphur content of the fuel to keep steps with the requirement of age. Then, in order to improve the environment further and taking into account the totalized conditions such as the relationship of combination with the adjacent Toho Petroleum Oil Co., Ltd. and fuel affairs, we decided to install a flue gas desulphurization plant belonging to the largest class in Japan as an effective means to lowering the sulphur content. Installation work was started on Oct. 17, 1974, and building work was continued for more than year and a half since then. The No.1 unit passed the per - operation test on April 8, 1976 and No.2 unit on June 25, 1976.

Both units have been and are in favorable operation.

The units will be described briefly here.

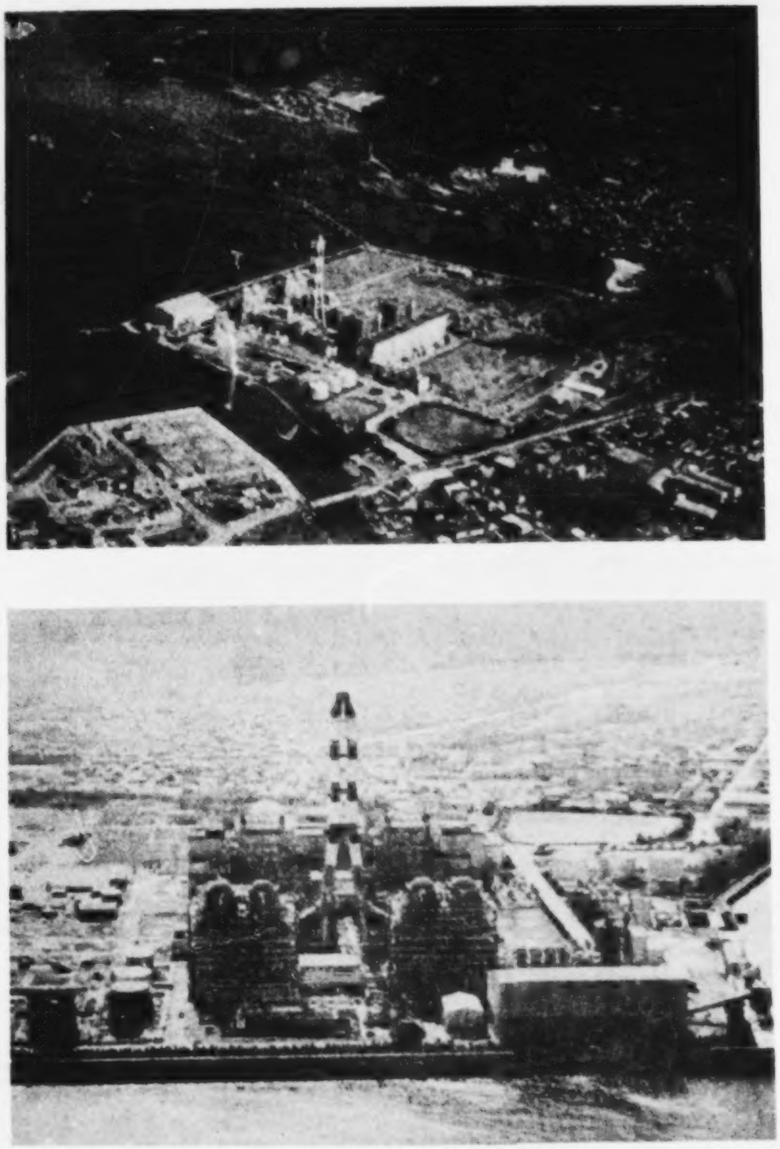
## 1. Outline of facility

Kind of unit Wet type lime-gypsum method
Amount of gas processed : $1,200 \times 10^3$ $Nm^3/h$
(Total amount of flue gas for 375,000 kW is processed)
Desulphurization factor : 90 % or more
Absorbent source material : Quicklime
Amount of source material used: About 60,000 tons/year
(Nos.1 and 2 units)
Byproduct : Gypsum
Amount of byproduct produced : About 180,000 tons/year
(Nos.1 and 2 units)
Flue gas reheating system : After burner system
Installation area : About 29,000 $m^2$
Total cost of construction : About 16,000,000,000 yen
(Aprox.64 million dollars)
(Nos.1 and 2 units)
Manufacturer : Mitsubishi Heavy Industries Co., Ltd.

## 2. Process

This unit accepts quicklime (CaO) as the source material and prepares from it the absorbent ($Ca(OH)_2$) solution. This solution is used to rinse the flue gas from the boiler to remove SOx content and recover gypsum ($CaSO_4.2H_2O$) as the byproduct.

The flow chart of the unit is attached at the end of this booklet



Owase-Mita Power Station and its surrounding viewed from air.

2-1 **Material accepting storing facility**

Since the material lime is dangerous it is carried by special dump trucks, delivered directly to the hopper, sent from the bottom of the hopper to the lime storing tank by using various conveyors and stored there temporarily.

The storing capacity is 1100 $m^3$. The tank capacity was designed as the capacity for 5 day's use, taking into account the holidays and road accidents.

### 2-2 Absorbing liquid preparation process

The quick lime is picked up from the storage tank, weighed, and then supplied to the lime mixing tank. There the lime is mixed with supernatant supplied from the gypsum thickener and digested to form milk of lime. The milk of lime is sent to the milk-lime thickener to classify the digestion residue. The over flowing liquid is taken out continuously and sent to the second absorbent reservoir as an absorbent 5 % in concentration. The digestion residue is taken out from the bottom of the thickener, crushed vertical tower mill, and all is used as the absorbent.

### 2-3 Flue gas cooling process

The flue gas of the boiler undergoes humidification, cooling, and dust removal in the cooling tower. The gas temperature, which is some 150 ℃ at the inlet, decreases to 55 ℃ at the outlet.

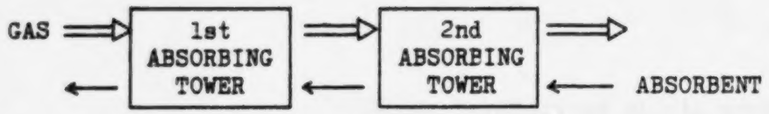
This process makes the desulphurizing reaction in absorbing process advantageous by decreasing the gas temperature and the same time, by saturating the moisture, plays a role of preventing the local condensation of slurry which is caused by the vaporization of the moisture in the absorbing unit.

### 2-4 Absorbing process

The gas that has passed through the cooling tower is washed with absorbent and removed of $SO_2$ here.

Grid filling type of simple cooling tower is used because of its advantage of having a large capacity factor of $SO_2$ absorption, small pressure loss, high performance stability, and being easily scaled up.

Two absorbing towers, installed in series with the gas flow, are employed in this unit in order to satisfy the $SO_2$ absorbing factor and Ca utility factor.



The main purpose of the 2nd absorbing tower is the removal of $SO_2$. The pH of the absorbent is set at 6.5 to remove most of the $SO_2$.

The purpose of the 1st absorbing tower is the role of making the unreacted Ca component in the absorbent used in the 2nd absorbing tower react again rather than $SO_2$ removal.

In the case where lime slurry is used to wash the gas, the most important practical problem is the prevention of scale adhesion. Scale is defined as the adherence of gypsum formed by the reaction between a portion of calcium sulphite and the oxigen contained in the waste gas to the grid and inner walls of the tower. Since in this unit various countermeasures are being taken, a smooth operation is continued.

Although calcium sulphite is formed by the main reaction of $SO_2$ absorption as shown in formula (1), one portion is oxidized to gypsum as shown in formula (2).

$$Ca(OH)_2 + SO_2 + H_2O \longrightarrow CaSO_3\ {}^1/_2H_2O + H_2O \quad \cdots\cdots (1)$$

$$CaSO_3\ {}^1/_2O_2 + H_2O \longrightarrow CaSO_4\ 2H_2O + H_2O \quad \cdots\cdots (2)$$

## 2-5 Oxidation Process

Calcium sulphite slurry is fed and compressed air is blown into the oxidation tower, where calcium sulphite is oxidized to form gypsum as shown in the reaction formula (2).

To cause oxidation to take place with the highest efficiency a rotary atomizer is installed on the bottom of the oxidation tower in order to float up very minute air bubbles through the slurry.

The gypsum liquid is controlled to below pH4. Sulphuric acid is added when the pH is higher. Since two absorbing towers are used in this unit the Ca utility factor is almost 100%, and the pH adjusting system is almost unused.

## 2-6 Filtration process

The gypsum slurry extracted from the bottom of the oxidation tower is condensed in the thickener sent to the squirrel-cage centrifugal separator as a 25% concentration fluid to be dehydrated. The moisture content of the gypsum is 10% or less, pH value is neutral, and the purity is 98% or more.

The overflown liquid of the thickener and the filtrate of the centrifugal separator are sent to the absorbent preparating process and reused in the digestion between it and lime.

## 2-7 Gypsum storing and delivering process

The gypsum that has been produced is carried to and stored in the gypsum warehouse by means of conveyors. The storing capacity was designed to be for 7 day's amount taking into account climatic condition etc. Marine transport of gypsum is being planned, and the quay allows up to a maximum of 1,500 ton vessels to approach.

Since the cargo-working is made in the day time in principle a ship loader having a maximum loading capacity of 230 tons/hour is installed on the quay and the conveyor carrying the gypsum to the loader is run through the inside a cylinder type closed duct.

## 2-8 Utilizing water, waste water treating

The amount of water used by this unit is about 3,500 $m^3$/day (2 units), the supply source is the surplus water from the deep well of the adjacent plant-TOHO PETROLEUM Co., Ltd. which is stored in a 3,500 kl tank installed in our yard. Abut 2,400 $m^3$/unit of liquid is circulating through the system and its control must be made with considerable care.

Spending a large amount of water this unit was so designed as to keep the water balance in the system by reusing as much water as possible.

Most of the waste water comes from the cooling system and it is treated by the waste water treating facility established within the system.

## 3. Installation schedule

Starting in February, 1974 we removed and moved 3 warehouses, 2 heavy oil tanks, light oil tank, modified appended pipings, and moved the ammonia tank to secure the installation site of the desulphurization plant. We also made geological survey and preparation work for electric power facility for engineering work.

This engineering schedule is as shown below.

| | No.1 unit | No.2 unit |
|---|---|---|
| Foundation work | Oct. 17, '74 | Same as left |
| Machine installation | Feb. 10, '75 | Mar. 28, '75 |
| Electric power reception | Sep. 18, '75 | Same as left |
| Flue gas passing | Dec. 26, '75 | Mar. 4, '76 |
| Commercial running | Apr. 8. '76 | June 25, '76 |

A period of about 10.5 months was spent between the installation of the units and the time of passing the flew gas . The scale of the unit was large, the kinds of work were many and the number of subcontractors was numerous. Moreover, almost all works were concentrated around the cooling and absorbing tower and the schedule was made severer by the following additional requirements.

(a) The lining of the cooling and absorbing tower and the inner path of the flue duct were made being always influenced by weather during the work.

(b) Since the lining pipe was the main subject of piping, installation of on-site fitting pipes such as the piping of coupling section could not be made until the completion of the lining of the main body.

(c) There were many rainy days.

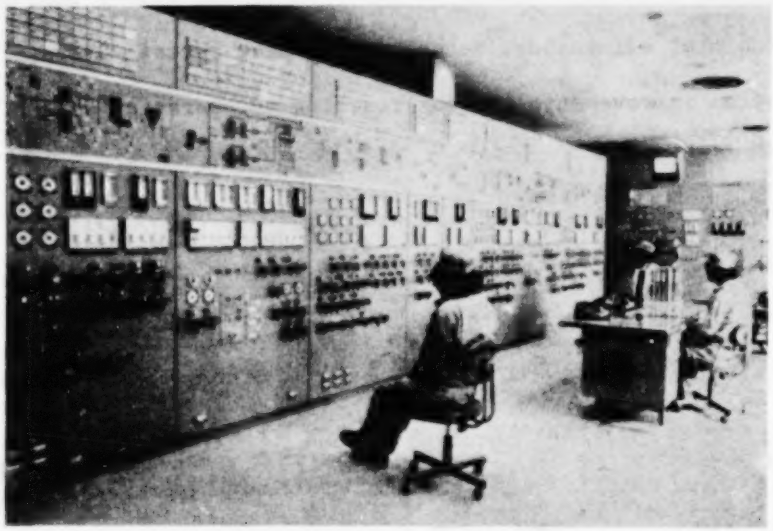
## 4. Electrical facilities

The power consumption of two desulphurization units is about 20,000 kW, and it was necessary to secure highly reliable electric wires. However, since the already existing power supply facility was insufficient in capacity it was determined to receive power from the 77 kV bus of the substation additionally installed. A transformer was installed on the desulphurization unit and a 200 $mm^2$ CV triplex cable is used, buried underground, to connect them.

Since the protection pipe has many bendings and its total length was 530 m, the EFLEX pipe, which is easy to lay, was used.

One unit of transformer was used common to Nos.1 and 2 units. Employment of 27/13.5 + 13.5 MVA 3 wire wound type made the short-circuit capacity small and MBB of small cut-off capacity (350 MVA) was used. No special stand-by power supply was installed because of the high reliability of the power supply. The emergency power was designed to be supplied from the existing diesel generator.

As for the DC power supply only a 125 V 1000 AH capacity one was used to operate those devices necessary to be operated assuredly immediately after the power failure.



Control room of the FGD plants

## 5. Control method

A control room common to Nos.1 and 2 desulphurization units having facilities capable of conducting concentrated operation and supervision of Nos.1 and 2 units by using 4 operators. The central control board was a vertical divided board arranged for each reaction group which is economically advantageous.

To make the performance of desulphurization unit to 450 x $10^3$ $Nm^3$/hour (equivalent to 125,000 kW) to 1200 x $10^3$ $Nm^3$/hour (equivalent to 375,000 kW) in waste gas amount and enable to follow the change in gas amount of 40 x $10^3$ $Nm^3$/min. (equivalent to 10,000 kW), the coordination of the control with the boiler load, a method in which the pressure at the outlet of the electrical dust precipitator, which is the junction point, is controlled to the pressure setting value determined by the load, was employed.

## 6. Actual results of running

Total duration of operation of No. 1 and No. 2 is 11,090 hours (No. 1) and 9,680 hours (No. 2) as of the end of September 1977 since their startup in April (No. 1) and in June (No. 2) in 1976.

Even though during the initial period following the startup, troubles occurred resulting from such causes as abrasion of the slurry piping and clogging of the mist eliminator, such troubles have recently been eliminated through operation improvements thereby reaching an operation rate of almost 100 percent.

The operation conditions may be outlined as follows:

(as of the end of September 1977)

| | | Startup - March 1977 | April 1977- Sept. 1977 | Total |
|---|---|---|---|---|
| Operation time of boiler (hr) | No. 1 | 7,384 | 4,122 | 11,506 |
| | No. 2 | 5,375 | 4,386 | 9,761 |
| Operation time of FGD (nr) | No. 1 | 6,977 | 4,106 | 11,083 |
| | No. 2 | 5,290 | 4,386 | 9,676 |
| Operation rate of FGD (%) | No. 1 | 94 | 99.6 | 96 |
| | No. 2 | 98 | 100 | 99 |
| Shutdown due to FGD trouble (times) | No. 1 | 2 | 1 | 3 |
| | No. 2 | 0 | 0 | 0 |
| Duration of shutdown due to FGD trouble (hr) | No. 1 | 242 | 6 | 248 |
| | No. 2 | 0 | 0 | 0 |
| HS fuel consumption (kl) | No. 1 | 550,000 | 310,000 | 860,000 |
| | No. 2 | 420,000 | 340,000 | 760,000 |
| Gypsum production (ton) | No. 1 | 85,000 | 43,000 | 128,000 |
| | No. 2 | 84,000 | 49,000 | 133,000 |
| Principal cause of shutdown due to trouble | No. 1 | 1) Leakage due to abrasion of the slurrypiping.<br>2) Clogging of the mist eliminator. | 1) Leakage due to abrasion of the slurry piping. | |
| | No. 2 | | | |

Principal problems so far experienced were as follows:

(1) Clogging of the mist eliminator

There were instances where the trains were stopped alternately to be cleaned in turns because the differential pressure tended to increase owing to gypsum scale that deposited on the elements of the mist eliminator during the initial period following the startup.

(2) Slurry piping

Leakage through the slurry piping and valves due to local abrasion was detected particularly in the parts that were subjected to high temperatures. Thus, the pipeline was modified in order to facilitate maintenance.

(3) Absorbing tower

Although partial clogging of the internal grid was seen, it did not lead to malfunction in particular. Cleaning of the grid was performed once annually at the time of periodical inspection.

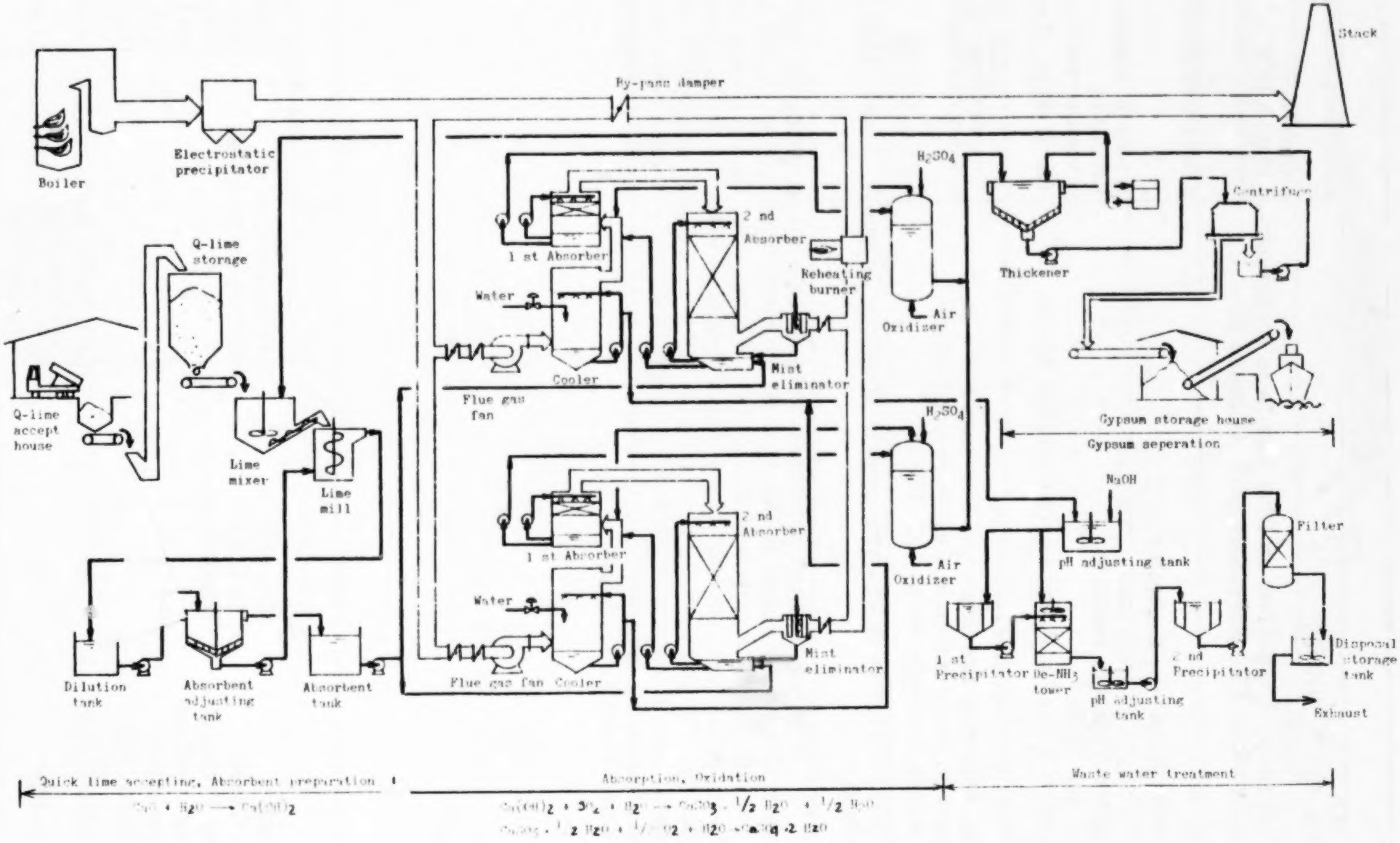
(4) While clogging of the filter element of the gypsum separator (centrifugal machine) occurred frequently during the initial period following the startup, its occurrence was brought to a minimum by employing filter element of a different type and changing the operation method.

## Summary

The unit, which was completed by investing a large capital, is different from the conventional power generating plant and appears to be a large chemical plant. In order to operate new devices with a few operators, there may arise many problematic points. However, if the desulphurization unit continues stable operation over a long period of time it will do its duty as a public pollution preventive unit and serve to accelerate the site planning of power supply facilities. This may be the best desired result. We are intending to make effort for maintaining the stable operation.

Although the utilization of gypsum is still low, since its utilization is being investigated eagerly in the related fields, we are expecting good results and, at the same time, hoping those concerned will give as further understanding and aid.

**Flow sheet of lime/gypsum FGD system**
**on Owase-Mita Station (Nos. 1, 2 unit)**



$CaO + H_2O \longrightarrow Ca(OH)_2$

$Ca(OH)_2 + SO_2 + H_2O \longrightarrow CaSO_3 \cdot 1/2\,H_2O + 1/2\,H_2O$

$CaSO_3 \cdot 1/2\,H_2O + 1/2\,O_2 + H_2O \longrightarrow CaSO_4 \cdot 2\,H_2O$